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DEVELOPMENT OF LOW COST CONTACTS TO SILICON SOLAR CELLS

FINAL REPORT

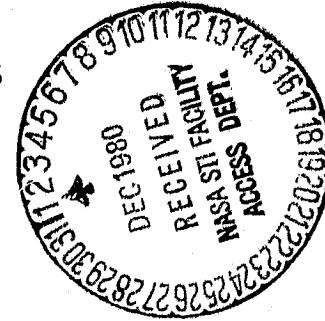
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JPL CONTRACT NO. 955244



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ABSTRACT

This report is a summary of work done on the development of a copper based contact system for silicon solar cells. The work has proceeded in three phases:

PHASE I:

Development of a copper based contact system using plated Pd-Cr-Cu. Good cells were made but cells degraded under low temperature (300°C) heat treatments.

PHASE II

The degradation in Phase I was identified as copper migration into the cells junction region. A paper study was conducted to find a proper barrier to the copper migration problem. Nickel was identified as the best candidate barrier and this was verified in a heat treatment study using evaporated metal layers.

PHASE III:

An electroless nickel solution was substituted for the electroless chromium solution in the original process. Efforts were made to replace the palladium bath with an appropriate nickel layer, but these were unsuccessful.

150 cells using the Pd-Ni-Cu contact system were delivered to JPL. Also a cost study was made on the plating process to assess the chance of reaching 5¢/watt.

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INTRODUCTION

This contract involves the evaluation of the technical feasibility and effective cost of a copper plated contact system for the manufacture of solar cells for high volume production of low cost solar array (LSA) modules.

Contacts have been identified as one of the most important but also one of the most expensive steps in making solar cells. Presently, space and terrestrial cells are made with the standard titanium-palladium-silver contact system developed in the early sixties. This system, though expensive, has shown long-term reliability and presently is the only contact system believed to be able to last the twenty year lifetime goal, as described by the LSA project. Studies show that cell metallization is an area where large reductions in cell process costs can be obtained. The present Ti-Pd-Ag contacts are evaporated under a vacuum, which alone, mainly due to the low throughput, is an expensive process. Also, metals like silver which are currently used in thicknesses of 3-10 microns are very expensive, and especially so when coupled with the large amount of wasted metal involved in the evaporation process. Therefore a new contact system should (A) use a high through-put technique, (B) should use a metal or metals that are inexpensive as compared to silver as the main current carrier, and (C) should have very low wastage of metals.

There are only two candidate contact techniques that meet this criteria. First there is the print-on-contact. This method uses a silk-screen which in conjunction with a conductive ink, to print the contacts on the cells in the desired pattern. The printed ink, next, has to be sintered at temperatures ranging from 450-750°C depending on the formulation of the ink and the cell processing sequence to obtain the desired properties. Reliability has been the major problem with this technique since control of the silicon-

contact interface is very difficult. Also the printed cells have sometimes exhibited non-ohmic contacts, contact peeling problems, as well as degradation of the cells after the severe heat treatments required for contact curing. All present print-on contact inks contain a large percentage of silver making a low cost contact system difficult to obtain. Waste of the contact metal, though much lower than with evaporation, is still a problem, due to lack of control of the contact thickness, and wastage of the ink left on the silk screen. A second contact technique is electroless or electrolytic plating. Using a plating technique, metals are only deposited on the cell where required. The first layer of metal (the metal-silicon) interface) can be controlled to get good adhesion and good cell performance. Using standard semiconductor metals such as silver or nickel, plating has proven to be a reliable contact system.

This contract has involved a study of the use of copper as the chief current carrying conductor for solar cells, replacing silver. Since copper is easily plated and is relatively cheap, it is a prime candidate for achieving a low cost contact system.

During the last eighteen (18) months several copper based contact systems have been studied. Work originally centered on finding a plating sequence that would yield contacts that had good adhesion and delivered good cell performance. However, it was quickly shown that diffusion of copper into the silicon cells would present a severe long term performance problem. This problem was addressed by a redirecting of the program to find a barrier metal to reduce copper diffusion.

This program was originally started with the thought of showing why copper would work as a solar cell contact metal. With the rising cost of silver and the good results we have obtained on this program, we feel that a copper based plated contact system is the best low cost approach available and should be more deeply explored.

BACKGROUND

Historically, silicon solar cells were made first with plated contacts. The system used was deposition of nickel by electroless methods, followed by solder build-up to provide adequate conductance, and to provide an interconnectable contact area. Later, space-use cells modified this system (in improving adhesion, and also in providing an improved ohmic contact) by adding a thin ($\sim 500 \text{ \AA}$) layer of gold, also deposited by electroless methods.

As the space-cell requirements were made more demanding (minimum pull-strength increased above 450 gm per 0.02 cm^2 areas, need to contact highly polished surfaces, and very shallow junctions, and adaptability to welding), the contact structure was changed to an evaporated stack of titanium-silver. Later to increase moisture resistance, a thin layer of palladium was added between the Ti and Ag. This contact system has proved to be a satisfactory space-use contact for most missions, and has been adapted to masking methods capable of providing the closely spaced, narrow grid pattern now being used for space or concentrator-use cells. In some cases the silver has been deposited by evaporation, and the required thickness is obtained by electroplating. Many of the current terrestrial cells use this space contact system, mainly because of the already existing technology. Several other contact systems (all-Al, all-Ag, Ce-Ag, Cr-Au-Ag, Cr-Pd-Ag, Ta-Pd-Ag) have been tested but have not been used for reasonably large numbers of cells.

In addition, work has proceeded on various forms of metal pastes or inks, deposited mainly through silk screen masks. In a few cases, the paste has been dispersed in photoresistive matrices and can be patterned by photoexposure methods. These methods are still under intensive study.

The modified Au-Ni-solder system has also been used again for terrestrial panels.

Developmental work (at Motorola ⁽¹⁾) has also led to a Pd-Ni-solder system.

This was the context into which the present program fitted. A method was needed, which could retain the advantages of a plated system (effective metal usage, relatively inexpensive equipment) while including other favorable aspects, such as easy control and repeatability, compatibility with inexpensive masking systems. The contacts had to have required properties to form an efficient cell, including low contact resistance, good conductance, good adhesion, good corrosion resistance and good thermal cycling properties.

We will examine these requirements in more detail.

(a) Metal Choice

There are relatively few metals of sufficient conductance (for reasonable thicknesses); these are silver, copper, aluminum and gold. If greater thicknesses are tolerable, other elements like Mg, Ni, Rh, Mo, W, or Cr, Pd, Nb, Ta have fair conductance, but are mostly ruled out because of difficulty of application or other properties. Also, some combinations (such as Sn-Pb-solders) can be used in relatively large thicknesses.

Of the four major conductors for the cost goals required, gold and silver were ruled-out because of cost, and aluminum also, because of the difficulty in plating methods (mostly only non-aqueous solutions have been successful) and also because of present reluctance to develop simple interconnect methods.

This left copper as a candidate metal, and for this reason, this program was initiated to explore the promise and problems resulting from choice of copper as the major metal constituent in cell contacts. Certainly the conductance of copper is most competitive. Copper can be of reasonably low cost, and an extensive technology exists for plating copper both by electroless and by electroplating methods.

(b) Contact Resistance

The contact resistance between silicon and metal (such as copper) is determined by two factors: the doping level of the silicon surface, and the detailed band properties of the metal, determining the Fermi level position, and the resultant contact potential. For silicon, however, the surface states can make the latter metal properties less predictable in determining the contact resistance, and in practice it is usual to resort to empirical determination of the actual contact potential resulting from a given silicon surface condition, and method of deposition of the metal.

It is customary to assume that the silicon slices requiring contacts will probably have N+ and P+ surfaces, both fairly highly doped, and already formed before contact application. We have used such slices in our program.

If empirical tests show that for given silicon surface conditions, a metal does have too high a contact resistance, often a satisfactory reduction in this resistance, often a satisfactory reduction in this resistance can be provided by use of a thin interfacial layer of another metal, deposited directly on the silicon before applying the main contact metal. The Au used in the electroless Ni system served such a purpose.

Below we will discuss tests of several different metals as underlayers for copper; included in these thin metal layers are Au, Pd, Cr, and Ni.

(c) Contact Adhesion

No matter how attractive the conducting properties of any metal contact system, it is essential that the contacts have good adhesion to the silicon. This is necessary, to ensure ease of handling into an array, and stability in operation.

The contact adhesion is determined by two factors, the surface finish, and the metal bonding mechanism at the surface. In general, rougher surfaces promote better adhesion for plated systems; thus use of a textured silicon surface (a competitive low cost method for processing silicon slices) has been assumed, although early tests have used fairly well polished surfaces. The bonding strength between silicon and metals is enhanced by use of a very clean silicon surface (and metals) and in some cases by relatively mild heat treatments (sintering) to consolidate the bonded interface. In some cases, the bonding is improved by use of a thin interfacial layer of the same type required to reduce contact resistance, and this approach has been used here in early studies of plating onto polished surfaces.

(d) Stability in Operation

There are three main possible causes of cell deterioration in practice. These are the chances of failure under thermal cycling, a mechanism minimized by choice of metals matched to the silicon, by providing high contact adhesion, or by restriction to thin metal layers. There is also the chance of corrosion, and this must be checked experimentally for the particular combination of cell contacts and interconnect metals.

Finally, there is the chance of cell degradation because some of the metal contact components can migrate to regions in the cell where they can reduce cell efficiency. It is this latter possibility which has often been invoked for copper, because of its well known high diffusivity (diffusion rate), so that even at relatively low

temperatures, copper atoms can move fairly long distances in the silicon. On the other hand, large quantities of copper have been introduced into bulk silicon without much loss of cell output.⁽²⁾ Thus again, empirical experimentation is needed to choose between these possibilities. In practice a set of carefully performed tests, using gradually increased temperature-time schedules, can identify the probability of such degradation by monitoring the cell efficiency resulting from this series of heat treatments.

There is an additional factor which can alter this possible mode of degradation. This factor involves the use of another thin interfacial layer of another metal, and above we have seen that such a layer may be needed to reduce contact resistance and to improve contact adhesion. The use of such a "barrier" metal could retard or prevent the motion of copper into silicon.

With this background, the approach to be used in the program can be better understood.

PROGRAM DETAILS

Cell Material

Slices of (100) oriented silicon were used. The P-type silicon had resistivities in the 7-14 ohm-cm range. Diffused layers were made using POCl_3 source at 850°C yielding sheet resistance ~ 25 ohms/ \square . All cells utilized an aluminum alloyed back surface field. Early tests were conducted on 2x2 cm cell sizes while the later tests were the cells of 2 $\frac{1}{4}$ " and 3" in diameter.

Plating Variables

The proposed program suggested using commercially obtained electroless copper plating solutions (preceded by sensitizing processes) to form a thin conducting layer

$\sim 1\mu\text{m}$ thick. The variables that were studied were:

- (i) Solutions differing in chemical composition, pH and temperature.
- (ii) Different sensitizing treatments.
- (iii) Surface preparation of the silicon.

Also the effect of these variables on plating rate, contact resistance, and adhesion were studies.

In addition, an understanding was sought of the basic mechanisms controlling the plating processes. Reference was made to the large body of published research, to confirm if our results were consistent with the current level of theoretical understanding.

Simultaneous N+ and P+ Plating

Efforts were directed toward plating the front and the back of the cell simultaneously. This proved to be very practical when using the electroless plating bath and no major problems were found.

Contact Build-Up

Earlier tests with electroless plating showed that the process tended to be self-limiting in that when the silicon surface had a reasonable thickness of metal ($\sim 1\mu\text{m}$) deposited, the tendency for further build-up was reduced. For solar cells contact thickness around $4\text{-}6\mu\text{m}$ are generally used.

To obtain thicker layers, two methods were evaluated:

- (a) Application of molten solder, followed by a reflow and pressing operation.
- (b) Use of electrolytic plating to build-up contact thickness.

Heat Treatments

The effect of various heat treatments on the contact properties were tested. The goal was achieving the optimum combination of overall cell properties, achieved if possible by a single heat treatment.

This was the basic direction of the program in Phase I. (October 15, 1978 to May 31, 1979).

Phase II (June 1, 1979 to January 15, 1980) involved a change of direction of the original program due to new problems occurring at the end of Phase I. The problem involved the shunting of the cells due to low temperature copper diffusion. A contact system was developed in Phase I which used a Pd-Cr-Cu plating sequence. Cells of good electrical properties were made but when sintered at 300° in nitrogen for 5 minutes, they would degrade severely. Phase II was directed toward solving this problem.

Paper Analysis

A literature search was conducted to evaluate copper diffusion through different metallic barriers in an effort to find a platable metal that would stop the copper migration. Also efforts were made to relate these results to a twenty year lifetime.

Test Matrix

Utilizing the results from the paper analysis a contact study was set-up to evaluate different metallization systems under controlled conditions. For this reason only evaporated metals were used. Four square centimeter cells were used with the different metal layers of varying thicknesses over a range of sintering temperature and times. Changes in the cells V_{oc} , I_{sc} , CFF and dark forward IV characteristics were observed.

Plating Mask

A search was also conducted for a low cost plating mask to replace the photoresist mask on the original process. It was hoped the mask could also offer increased control with the copper deposition and possibly also provide an inexpensive anti-reflection coating for the cell.

Corrosion Protection

Since copper is relatively reactive, work was done to protect the cell's contact surface. The plan was to coat the copper surface using an electroless bath.

Process Modification

Phase III (January 15, 1980 to April 30, 1980) was directed toward a final effort to simplify the plating process further. This was to be accomplished by elimination of one of the electroless plating baths.

Plated Cell Sintering Test

After the plating sequence was finalized 150 cells were made for delivery to JPL. Extra cells from this group were used in a contact sintering test in an effort to establish the reliability of the contact system.

TECHNICAL DISCUSSION

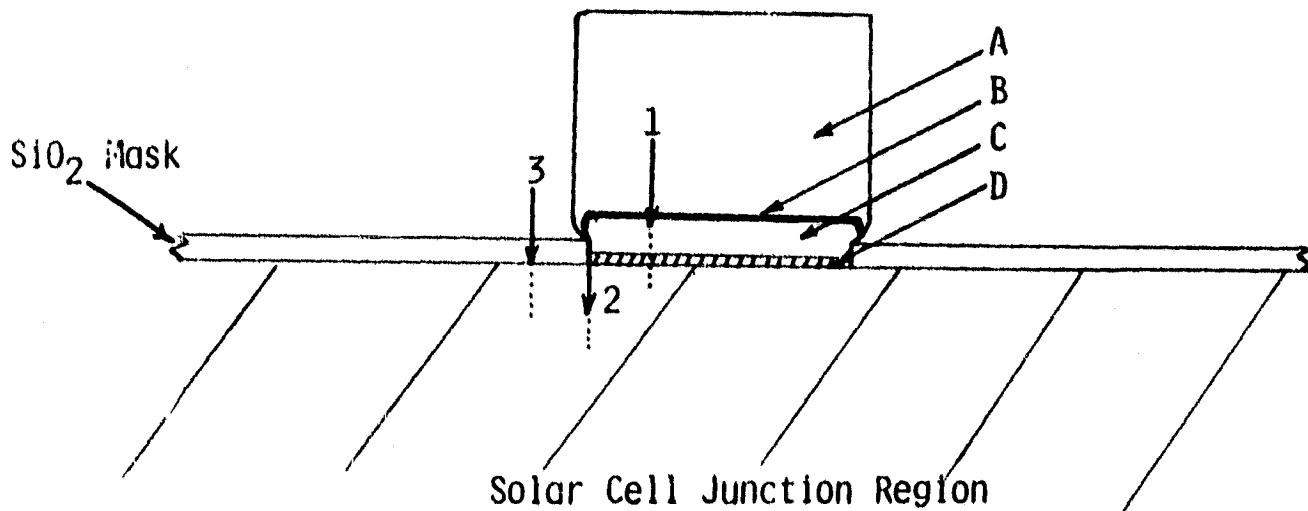
During the duration of the contract a number of important observations were made mainly in dealing with copper as a solar cell contact material.

The contract was originally started with the thought of doing an exhaustive study to show explicitly why copper will not work as a solar cell contact material. Copper is well known to cause serious degradation problems with silicon devices throughout the semiconductor industry, so the possibility of success appeared to be remote.

Controlling Copper Migration

Though the first experiments dealt with plating copper directly on the silicon, by the end of the first phase of work a contact system had been developed that yielded high quality solar cells. The contact system used a thin layer of palladium (~50 Å), 2000 Å of electrolessly plated chromium, and then a thick (~5 μm) layer of plated copper. These cells though, were shown to degrade severely under heat treatments as low as 300°C for five minutes in nitrogen. Figure 1 shows all avenues of copper migration thought to be possible in causing the degradation problems. Mode one was identified as the diffusion of copper through the metallic barrier layer. This mode can be controlled by changing the barrier metal type, its thickness, and its relative density. (Plated layers will certainly be less dense than evaporated layers). Mode two was identified as edge leakage around the metallic barrier layer. (Here between the chromium layer and the plating mask). Mode three is identified as the possible diffusion of copper through the plating mask material. Since on the standard substrate for plating, the plating mask can also serve as an anti-reflection coating, the thickness of this mask is limited to 750-1,200 angstroms depending on the mask material (SiO₂, Si₃N₄, etc.). With such a thin layer, pinholes allowing direct diffusion of copper would cause serious cell degradation.

FIGURE 1
Modes of Copper Migration



NOTE: MODE 1: Migration through chromium layer
2: Migration at plating edge
3: Migration through plating mask

Layer A: Electrolytic copper
B: Electroless copper
C: Electroless chromium
D: Immersion Palladium

Work was directed toward preventing or eliminating these modes as possible copper degradation sources. This work is discussed the experimental section.

Silicon/Metal Interface Control

Even our early work showed that a major advantage which plating has over screen printed contacts, is the fine control of the silicon/metal interface. Without control of this interface cells will possibly show:

- (A) Poor adhesion of the contacts.
- (B) High contact resistance.
- (C) Poor process control in later plating steps.

This interface in our process is controlled by a thin palladium layer plated from an immersion type bath. (Adhesion was also enhanced if the palladium created a rough palladium surface.)

High Plating Rates

High plating rates are important for obtaining a high throughput process. However, high initial plating rates can cause adhesion problems. With electrolytic plating, very high rates cause the grain size of the deposited copper to greatly increase, causing poor adhesion. A slow plating rate in the first few minutes of plating yielded a very fine grain structure and good adhesion of the plated contact layer.

Edge Plating

When electroless baths are used, the exposed edges of the cells are plated also. (Usually the front masking material cannot adequately mask the edges also.) Therefore, there must be an edge clean-up step (etching or grinding) in the process to remove this excess metal.

EXPERIMENTAL PESULTS

Phase I

Copper Only System

The first plating experiments were conducted to test plating copper directly onto the silicon surface. This set of experiments only succeeded after using a palladium-tin sensitizer (Appendix B, Solution A) before plating on the cell, but the copper was not adherent enough for further test.

Gold-Copper System

The second plating system developed was a gold-copper system (see Appendix A). Gold was thought to be a good material to make the copper stick on the silicon and gold plating solutions were readily available. Later when a quick cost analysis showed a 500 angstroms layer, only on the back of the cell would cost about \$.08/watt in material cost alone, this direction of research was abandoned. A few adherent cells were made, however, leading us to believe a search for good sticking metal was the correct direction in the research.

Chromium-Copper System

A careful scan of the metals available for electroless plating in conjunction with their thermal expansion characteristics, suggested chromium would be the best material for this job. Since chromium is an alternative to titanium in evaporated contacts, the choice seemed an obvious one. The first electroless chromium bath (Bath A, Appendix C) was found to be hard to control and gave very non-uniform chromium layers. A second bath (Bath B, Appendix C) was found, which gave much better results when properly sensitized by the tin-palladium solution (Appendix B). This layer, however, had very poor adhesion before heat treating which led us to believe a better sensitizer was needed. The immersion palladium bath (Appendix E) developed by Motorola, gave a very promising

result when used with Bath B. Since the palladium layer left was very adherent and the new sensitizing bath was also void of tin, an element known to have low eutectic temperature with silicon, the research appeared to be headed in the right direction. With minor modifications, of the palladium bath, uniform and reliable chromium plating was now routine. After the chromium layer was plated, the cells were sintered and then plated in the electroless copper solution (Appendix B, Solution C). This commercial electroless copper bath was only used to make the electrolytic copper layer more adherent. The 500 angstroms layer generated from this copper bath made a very uniform and consistent layer for the electrolytic bath to plate. The thin electroless plated copper layer was then electrolytically copper plated to a thickness between 4-6 microns. Figure 2 shows a typical I-V plot of a cell made with the palladium-chromium-copper sequence (full sequence is shown in Appendix F). This cell had a CVD SiO_2 layer which led to about 25-30% increase in current from its antireflection effects. (This layer was used only as a plating mask, not as an optimum antireflection coating.)

Palladium-Copper System

Since the electroless palladium baths had been developed by Motorola, it was thought a palladium-palladium-copper cell should also be studied (see Appendix G). The cells were quickly made and Figure 3 shows a typical I-V plot of one of these cells. The only concern of using thick palladium for a contact metal is that palladium is relatively expensive. Other groups (such as Westinghouse) have also done work looking at the copper migration problem and have found palladium does not act as a very good barrier.

Another important test of contact quality is the contact pull test. In this test small wires were soldered to different areas of the cells (front and back). The cells were put in a special chuck where the wire could be freely pulled perpendicular to the silicon surface while the pull strength was being measured. Since the pull strength is directly

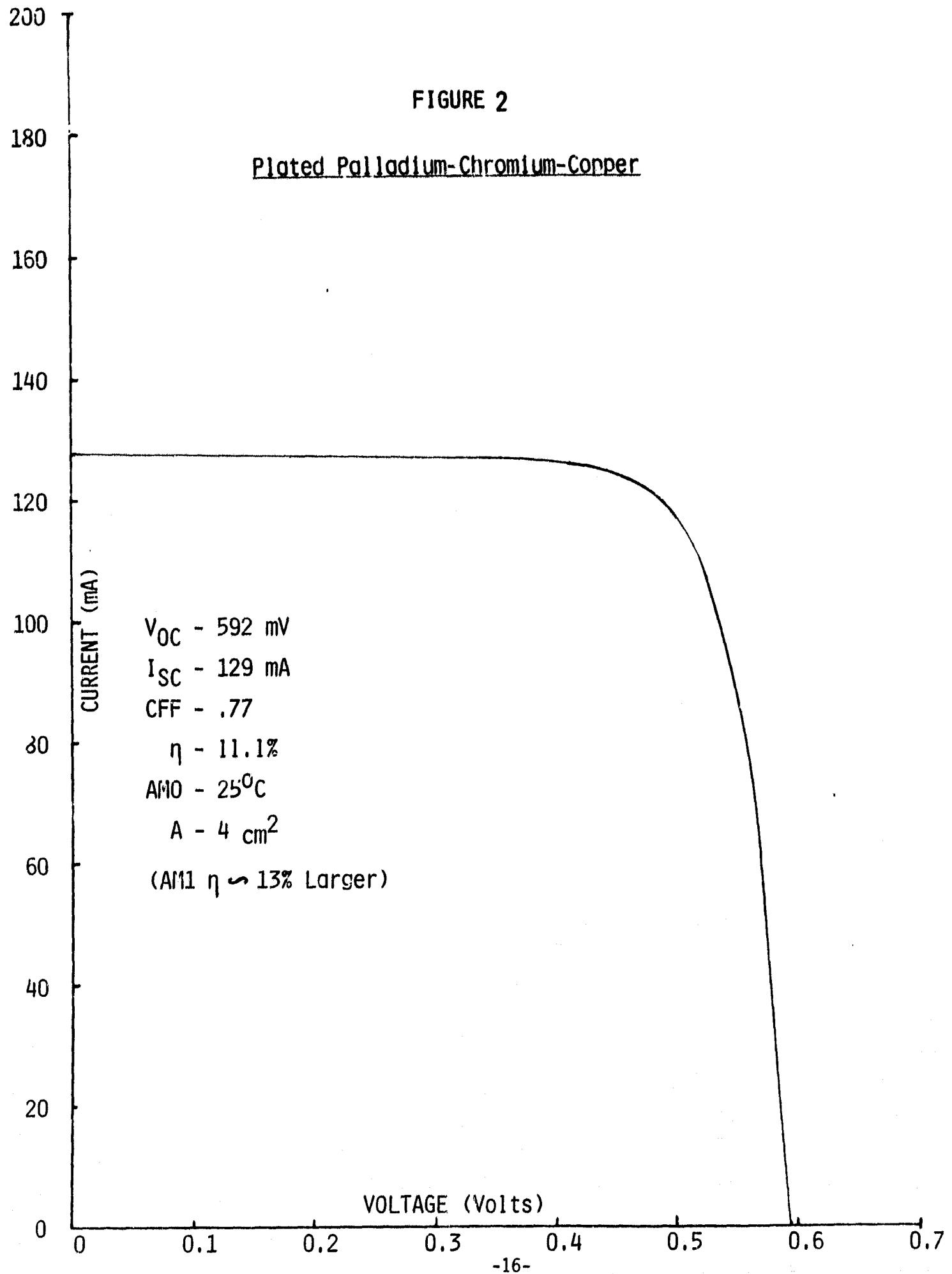


FIGURE 3
Plated Palladium-Palladium-Copper

CURRENT (mA)

$V_{OC} = 595$ mV
 $I_{SC} = 136$ mA
 $CFF = .77$
 $\eta = 11.7\%$
 $A_{H10} = 25^{\circ}\text{C}$
 $A = 4 \text{ cm}^2$
($A_{H11} \eta \approx 13\%$ Larger)

VOLTAGE (Volts)

TABLE I
CONTACT ADHESION

CONTACT TYPE	MODE	AREA	PULL STRENGTH	
			FRONT	BACK
Ti-Pd-Ag	Evaporated	.02 cm ²	200 gm*	236 gm [†]
Cr-Cu	Evaporated	.02 cm ²	117 gm*	250 gm [†]
Pd-Cr-Cu	Plated	.02 cm ²	83 gm*	220 gm [†]
Pd-Pd-Cu	Plated	.02 cm ²	170 gm*	280 gm [†]

*Pulled Some Silicon

[†]Cell Broke

Cell Substrate: 7-14 ohm-cm P-Type - Chemically Polished Front -
Al Alloyed Back

Cell data taken from five cell groups.

related to the area (assumed linear until the contact or the silicon breaks), the size of the soldered area was then measured after pulling and the pull adjusted to a constant $.02\text{ cm}^2$ area. Table I shows the results of the pull strength test on four different contact types. All tests pulled some silicon with the contact or broke the silicon samples during the pull. It is believed that if a textured front surface is used, better adhesion will be obtained.

Scaling Up the Final Process

With the palladium-chromium-copper system working on a small scale (plating on $2\times 2\text{ cm}^2$ cells), the next requirement of the contact was to scale up, to a size closer to a production type effort. We decided to use $2\frac{1}{4}$ " diameter cells. These cells would not require bath sizes as large as with 3" diameter cells, but the baths would still have to be increased in size by a factor of six. Even though the silicon quality was not the highest with the scaled-up baths, no fundamental problems occurred. The cells were processed in lots of ten (10), since our heat treating furnace could only accommodate five (5) cells at a time.

The immersion palladium bath worked just as before, even with the large number of cells processed. Over seventy-five (75) $2\frac{1}{4}$ " cells were sensitized in this one bath. The depletion rate of this bath appeared to be low.

The electroless chromium bath (when used successively) depleted very quickly. After only the first twenty (20) cells, the plating rate decreased several orders of magnitude. It was found, however, if 3.5 grams of sodium hypophosphite was added after every ten (10) cells the bath plating rate would remain relatively consistent. Up to forty (40) cells have been plated in one bath. But another problem appeared as this bath became older. The masked areas of the cell became plated with dark deposits of loose material. This appeared to be a problem stemming from the depletion of other chemicals

in the bath. Chromium baths typically can be used up to a week with proper replenishing of the used chemicals⁽²⁾.

The electroless copper bath worked repeatedly and did not seem to deplete during this test. One problem with the electrolytic copper bath involved the size of the power supply. With the present supply only a few cells could be plated at one time, but the size of this supply can be increased to plate a large number of cells at one time. Figure 4 shows a typical I-V plot from one of these large cells. The front electrode thickness was increased to 10 microns on this cell to lower the high series resistance. The photomask that was used was the only one readily available for the cell size. It was designed for a silver thickness of 10 microns for a good cell fill factor (CFF) (Plated copper, 15 microns thick, would yield a CFF of 77% with this mask). A new mask was designed that required only 5 microns of copper for cells generating a 74-76% curve fill factor. Table 2 shows a group of five cells taken in random from the forty (40) cells delivered to JPL. Only one cell, No. 4, was shunted. This is believed to be from an aluminum alloy problem, not from cell contact problems.

Evaporation Experiments

After the new plated contact system was well developed, the question of long term reliability of cells with copper contacts was still unresolved. Simple heating (400-500°C) of the plated cells reduced V_{oc} and CFF but sometimes the thick copper layer would peel (probably due to the sudden changes of temperature with the differences in linear expansion of the metals). It was decided in order to closely control the metal layers, that is to eliminate any plating variables such as thickness or bath impurities, a heat treatment test of evaporated chromium-copper system would be conducted. The first test (Test No. 1) was done on cells made previously as a comparison in efficiency of the plated cells. These cells were given a limited heat treat cycle with temperatures

FIGURE 4

PLATED PALLADIUM - CHROMIUM - COPPER

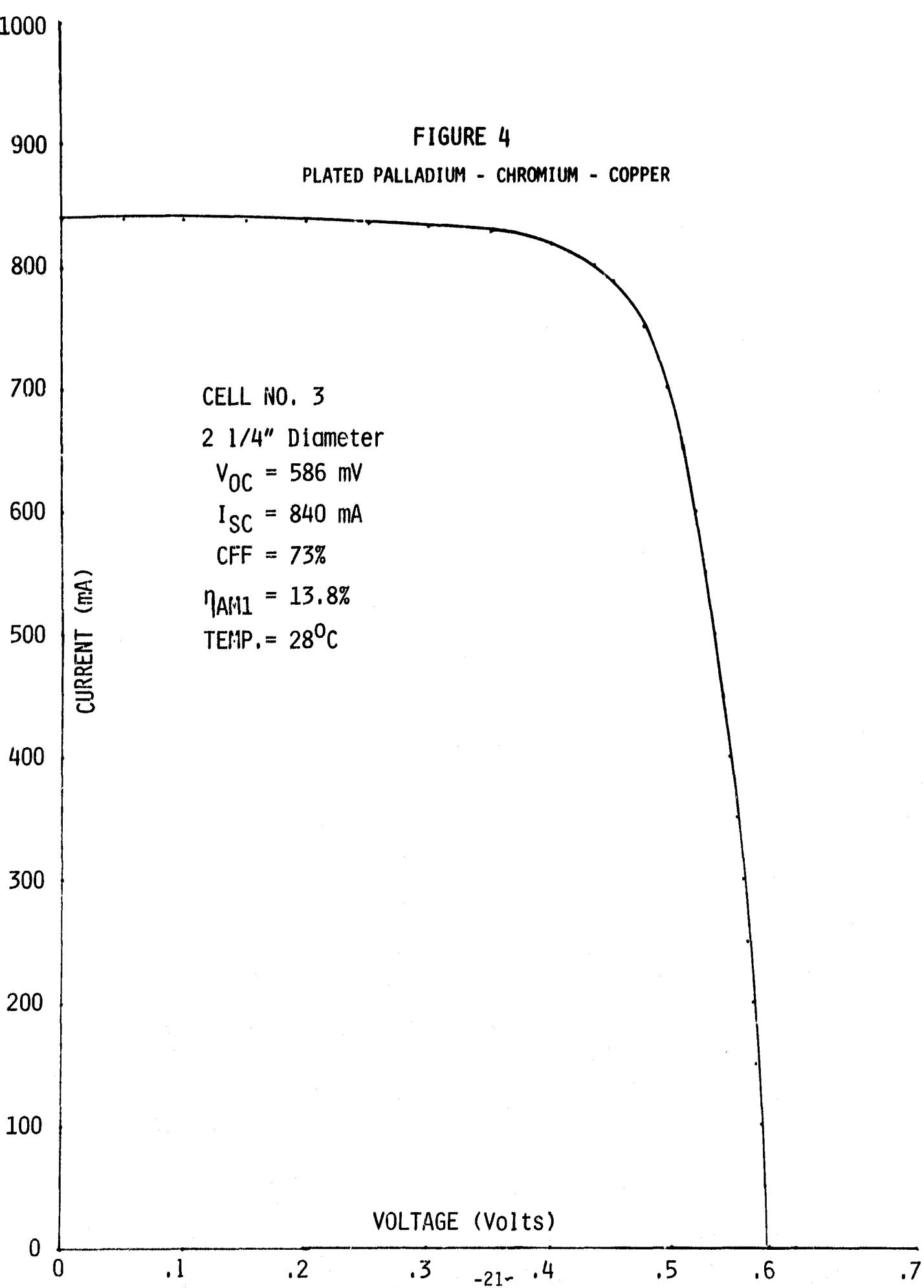


TABLE 2

SOLAR CELL ELECTRICAL DATA

CELL DESCRIPTION: 2 1/4" Solar Cells With Pd-Cr-Cu Plated Contacts

TEST CONDITION:
TEMPERATURE:

280C

No.	V _{OC}	I _{SC}	I _{SCB}	I _{SCR}	I _{Max}	V _{Max}	P _{Max}	CFF	η	AREA
	mV	mA	mA	mA	mA	mV	mW	%	%	cm ²
1	586	840	---	---	750	470	352.5	72	13.7	25.7
2	585	850	---	---	755	470	354.9	71	13.8	25.7
3	579	840	---	---	755	470	354.9	73	13.8	25.7
4	454	817	---	---	550	260	143	39	5.6	25.7
5	586	868	---	---	760	460	349.6	69	13.6	25.7

Cells had only approximately 30% current increase due to the CVD SiO_2 (only a plating mask). These are five cells taken in random from the forty (40) cells delivered to JPL.

TABLE 3

SOLAR CELL ELECTRICAL DATA

CELL DESCRIPTION: Cr-Cu Evaporated Contacts With Plated Cu Before Heat Treats (2x2 cm)

TEST NO. 1 (1:00 AMSTOLIS CLOTHING)

TEST CONDITION:
TEMPERATURE:

No.	V_{OC} mV	I_{SC} mA	I_{SCB} mA	I_{SCR} mA	I_{Max} mA	V_{Max} mV	P_{Max} mW	CFF %	τ s	AREA cm ²
A1	601	133.2	51.9	81.2	117.3	500	58.65	.73	10.9	4
A2	600	128	46.2	82	117	500	58.65	.76	10.8	4
B1	600	129.7	43	82	116.9	500	58.45	.75	10.8	4
B2	599	127.4	48.4	79	110.4	500	55.2	.72	10.2	4
C1	502	134.3	52.3	82.4						
C2	599	128.8	47	82	115	500	57.5	.75	10.7	4

These are 2x2 cm² cells with the standard plating substrates.

A - 400°C, 5 minutes in N₂
 B - 450°C, 5 minutes in N₂
 C - 500°C, 5 minutes in N₂

ranging from 400-500°C. Table 4 shows the cell data after the heat treatments. Some of the cells appear to remain about the same, where the others degraded severely. Since this test included only cells with plated copper, a more controlled test was needed. Table 5 shows the different contact cell groups and test parameters of Test No. 2. Notice there were two groups of each type contact system, chromium-copper and titanium-palladium-silver. One group used evaporated metals together with plated metals (copper or silver) while the other used evaporated metals only. The cell groups were marked C - for evaporated chromium-copper, CP - for evaporated chromium-copper-plated copper, T - for evaporated titanium-palladium-silver (2000 angstroms silver), and TP - for evaporated titanium-palladium-silver-plated silver. These four groups of cells were used to separate the effects of plating, namely the mode (3) (migration through the plating mask) shown in figure 1. Table 6 shows a summary of typical cells from each group after the 400 and 500°C heat treatment. The results show cells which indicate very little degradation with the 400°C heat treatment. But with the 500°C heat treat, degradation was apparent from all the cells with copper contacts. Cells that had plated copper, degraded much worse than the evaporated-only chromium-copper cells, indicating it was bad for the copper to directly touch the silicon surface. Since even the evaporated chromium-copper showed some degradation, it was apparent that mode (1) (migration through the chromium layer) was operating with this contact test. Figure 5 is a forward bias dark I-V plot of typical cells taken from Test No. 2 heated at 400°C.

There appears to be little difference between the groups. Figure 6 shows the results from cells of the 500°C heat treating, indicating again that the copper cells degraded. Notice on Table 6, the red and blue current responses (I_{SC_R} and I_{SC_B}) were unchanged even after the severe 500°C heat treat, indicating no reduction of minority carrier diffusion length. From the dark IV data, and the constant generated current levels, conclusions of the effects of copper migration can be made. It appears that the

TABLE 4

SOLAR CELL ELECTRICAL DATA

CELL DESCRIPTION: Cr-Cu Evaporated Contacts With Plated Cu After Heat Treats (2x2 cm)
 Test No. 1 (1000 Angstroms Chromium)

TEST CONDITION:
TEMPERATURE:

二二

No.	V _{OC} mV	I _{SC} mA	I _{SCB} mA	I _{SCR} mA	I _{Max} mA	V _{Max} mV	P _{Max} mW	CFF %	%	%	AREA cm ²
A1	593	133	52.1	80.9	114	450	51.3	.65	9.5	4	
A2	594	128.4	47.1	81.5	114	495	56.4	.74	10.4	4	
B1	596	129.5	48.6	81.4	117	490	57.3	.74	10.6	4	
B2	593	127.4	48.9	78.5	109	480	52.3	.69	9.7	4	
C1	400	134.3	52.4	82	106	235	24.9	.47	4.6	4	
C2	593	129.3	47.9	81.5	114	485	55.3	.72	10.2	4	

These are 2x2 cm² cells with standard plating substrates. The cells were heat treated as follows: A 1000°C 5 min

A - 400°C, 5 minutes in N₂
B - 450°C, 5 minutes in N₂
C - 500°C, 5 minutes in N₂

TABLE 5
EVAPORATED CONTACT TEST NO. 2

GROUP NO.	CONTACT TYPE
1	Cr-Cu (1000 \AA Cr - 5000 \AA Cu)
2	Cr-Cu-Plated Cu (4-6 microns)
3	Ti-Pd-Ag (only 2000 \AA Ag)
4	Ti-Pd-Ag-Plated Ag (4-6 microns)

Sets from each group were heated at 400°C, 450°C, and 500°C for 5 minutes in Nitrogen.

Groups 1 and 3 plated-up after heat treatments for proper comparison.

NOTE: EACH SMALLER GROUP CONTAINED A SET OF 5 CELLS.

TABLE 6
SOLAR CELL ELECTRICAL DATA

CELL DESCRIPTION: Chromium-Copper Evaporated Heat Treat Tests (2x2 cm)
Test No. 2 (1000 Angstroms Chromium)

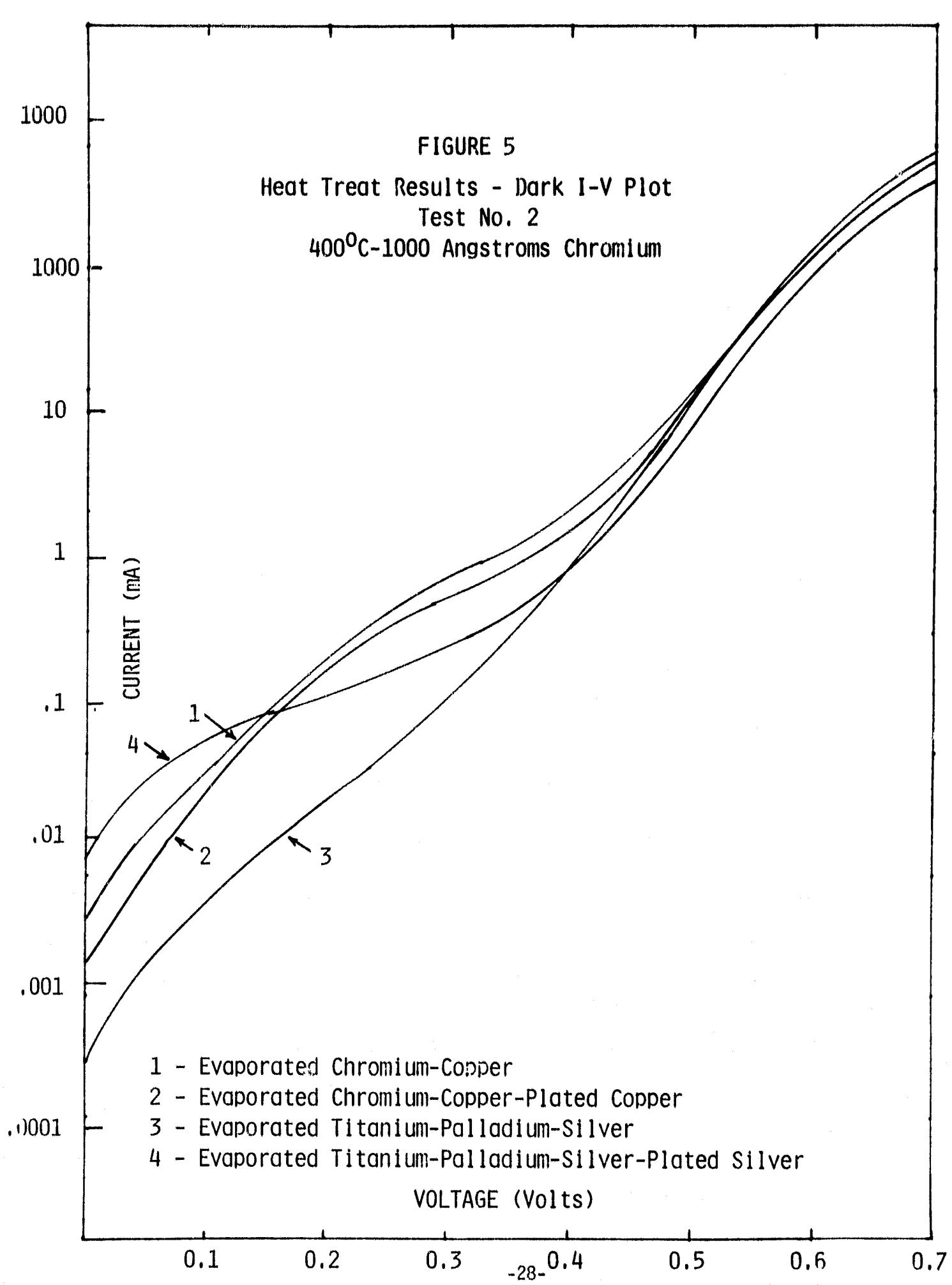
AMO

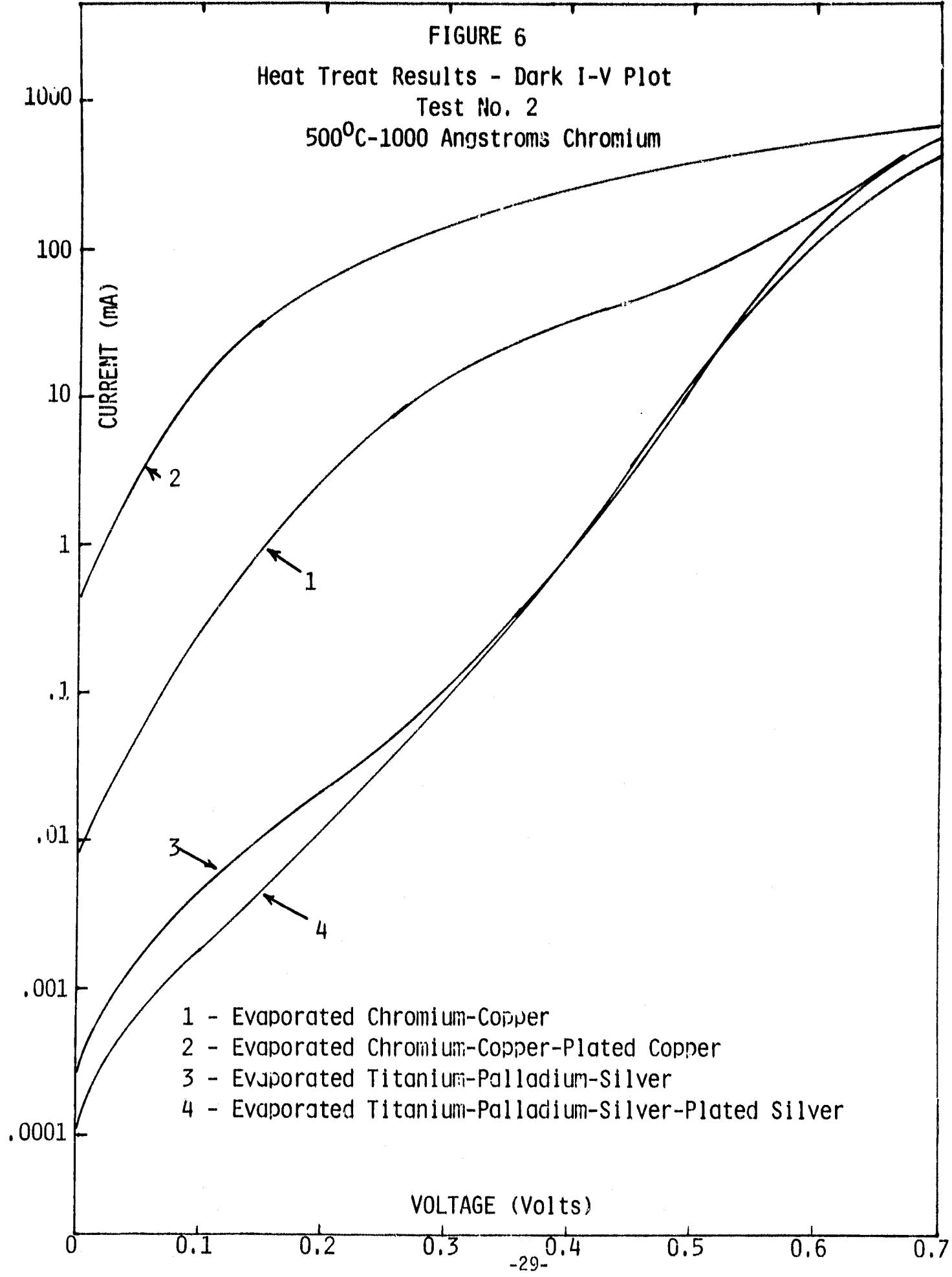
28°C

DATE: 23 March 1979

No.	V _{OC} mV	I _{SC} mA	I _{SCB} mA	I _{SCR} mA	I _{Max} mA	V _{Max} mV	P _{Max} mW	CFF %	E %	Area cm ²	Area
GROUP 1											
400°C	594	143	51	91	130	.5	65	.76	12	4	
500°C	554	141.7	50	92	104	.385	40	.51	7.4	4	
GROUP 2											
400°C	597	144	51.6	93	133	.495	65.8	.77	12.2	4	
500°C	302	141	50	90	103	.16	16.5	.39	3	4	
GROUP 3											
400°C	594	146	50	96.8	135	.495	66.8	.77	12.4	4	
500°C	597	148	51	97.6	136	.5	58.4	.77	12.7	4	
GROUP 4											
400°C	596	147.8	50	97.5	134	.495	66.3	.75	12.3	4	
500°C	595	146	53	93	132.5	.49	64.9	.75	12	4	

FIGURE 5
Heat Treat Results - Dark I-V Plot
Test No. 2
400⁰C-1000 Angstroms Chromium





SOLAR CELL ELECTRICAL DATA

CELL DESCRIPTION: Evaporated Test No. 3, Chromium-Copper - 2000A Chromium (2x2 cm)

TEST CONDITION: AM0
TEMPERATURE: 280°C

DATE: 9 May 1979

NO.	V _{OC} mV	I _{SC} mA	I _{SCB} mA	I _{SCR} mA	I _{Max} mA	V _{Max} mV	P _{Max} mW	CFF	η	z
GROUP 1										
400°C	591	138.4	47.0	92	122	460	56.1	69	10.4	
500°C	586	136.4	45.3	91	117	440	51.5	64	9.5	
GROUP 2										
400°C	590	138.3	49.2	89.6	128	495	63.4	78	11.7	
500°C	569	137.6	49.9	87.1	110	465	51.4	65	9.5	
GROUP 3										
400°C	595	140.8	47.7	93.4	130	500	65	78	12	
500°C	592	138.4	47.1	91.3	126	480	60.5	74	11.2	

1000

FIGURE 7

Heat Treat Results - Dark I-V Plot
Test No. 3
400°C-2000 Angstroms Chromium

100

10

1

.1

.01

.001

.0001

CURRENT (mA)



2
1
3

- 1 - Evaporated Chromium-Copper
- 2 - Evaporated Chromium-Copper-Plated Copper
- 3 - Evaporated Titanium-Palladium-Silver-Plated Silver

VOLTAGE (Volts)

0

0.1

0.2

0.3

0.4

0.5

0.6

0.7

FIGURE 8
Heat Treat Results - Dark I-V Plot
Test No. 3
500⁰C-2000 Angstroms Chromium

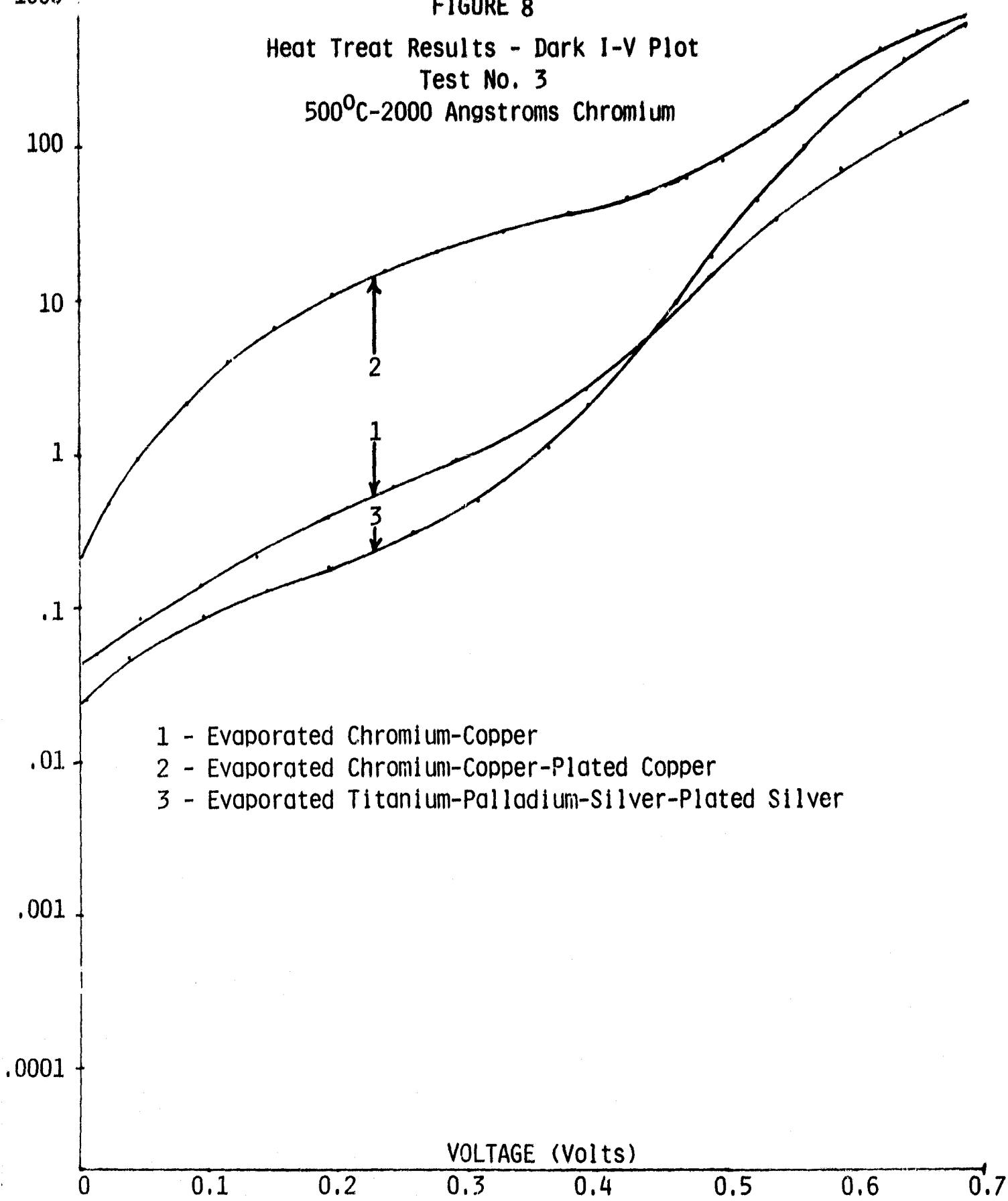


TABLE 8

COMPARISON OF TEST NO. 2 RESULTS TO TEST NO. 3 RESULTS IN CHANGE
OF VOC AND IN ABSOLUTE CHANGES OF THE FORWARD BIAS, DARK CURRENT
AT .3 VOLTS AND WITH DIFFERENT TEMPERATURES AND THE SAME THICKNESSES

TEST NO.	GROUP NO.	VOC (400-500°C)	DATA AT .3 VOLTS
2	1	29.2 mV	9.1 mA
	2	259.3 mV	199.3 mA
3	1	7.4 mV	.4 mA
	2	34 mV	29.5 mA

NOTE:

Group 1, Test No. 2: Cells have 100 \AA Cr-5000 \AA Cu

Group 2, Test No. 2: Cells have 1000 \AA Cr-5000 \AA Cu-4 Plated Cu

Group 1, Test No. 3: Cells have 2000 \AA Cr-5000 \AA Cu

Group 2, Test No. 3: Cells have 2000 \AA Cr-5000 \AA Cu-4 Plated Cu

NOTE: Each cell group had five cells.

copper is migrating and creating acceptor states in the depletion region of the cell. This would have the effect of lowering the V_{oc} as well as the reducing the curve fill factor. However, as noted, the lifetime of the silicon in the bulk and near the junction-region was unchanged as indicated by the red and blue response, respectively. Therefore, this series of tests indicate that copper when diffusing into a solar cell will quickly cause junction problems (states in the depletion region) and not carrier lifetime problems in the bulk region.

Test No. 3 was designed to look at the effects of the same tests in Test No. 2 but with an increase in thickness of the chromium layer to 2000 angstroms. Only groups 1, 2, and 4 were used from Test No. 2. Groups 3 and 4 in Test No. 2 were basically control groups. When little difference was seen between them, it was thought only group 4 would be needed as a control to Test No. 3. Table 7 shows a summary of the data for the 2000 angstroms chromium test. A full accounting of the data is in Appendix I. Figure 7 shows the forward bias dark I-V data for cells from Test No. 3 heated at 400°C . Notice as before there is very little change in the curves, especially at .3 volts region controlled by space charge effects. Figure 8 shows the same plots for cells heated at the 500°C level. The Group 1 cell showed a very small change in the current at the .3 voltage level as compared to the same plot in Task No. 2, Figure 6. The Group 2 cell again showed a large change at the .3 voltage level, but still smaller than the comparable plot from Test No. 2, Figure 6. Again the data seems to indicate that plated copper is touching the silicon surface caused by the poor plating mask. Table 8 shows a comparison of changes in V_{oc} over the temperature range and dark current at .3 volts for the different groups with the same thicknesses. This clearly shows a decrease in the changes caused by the 500°C heat treat by the increased thickness of the chromium.

From these results, it became apparent for a copper based system to work over a long period of time, a suitable metallic barrier would have to be found to stop the copper

from migrating to the silicon surface.

Phase II

The work in Phase II was set-up to address this problem of finding a suitable barrier layer.

A literature search was conducted to locate papers dealing with copper diffusion and/or interactions with different metallic barriers. It was preferred that the search be restricted to papers dealing strictly with diffusion studies using thin films, but during the search it was found that only a limited amount of data on thin films are available.

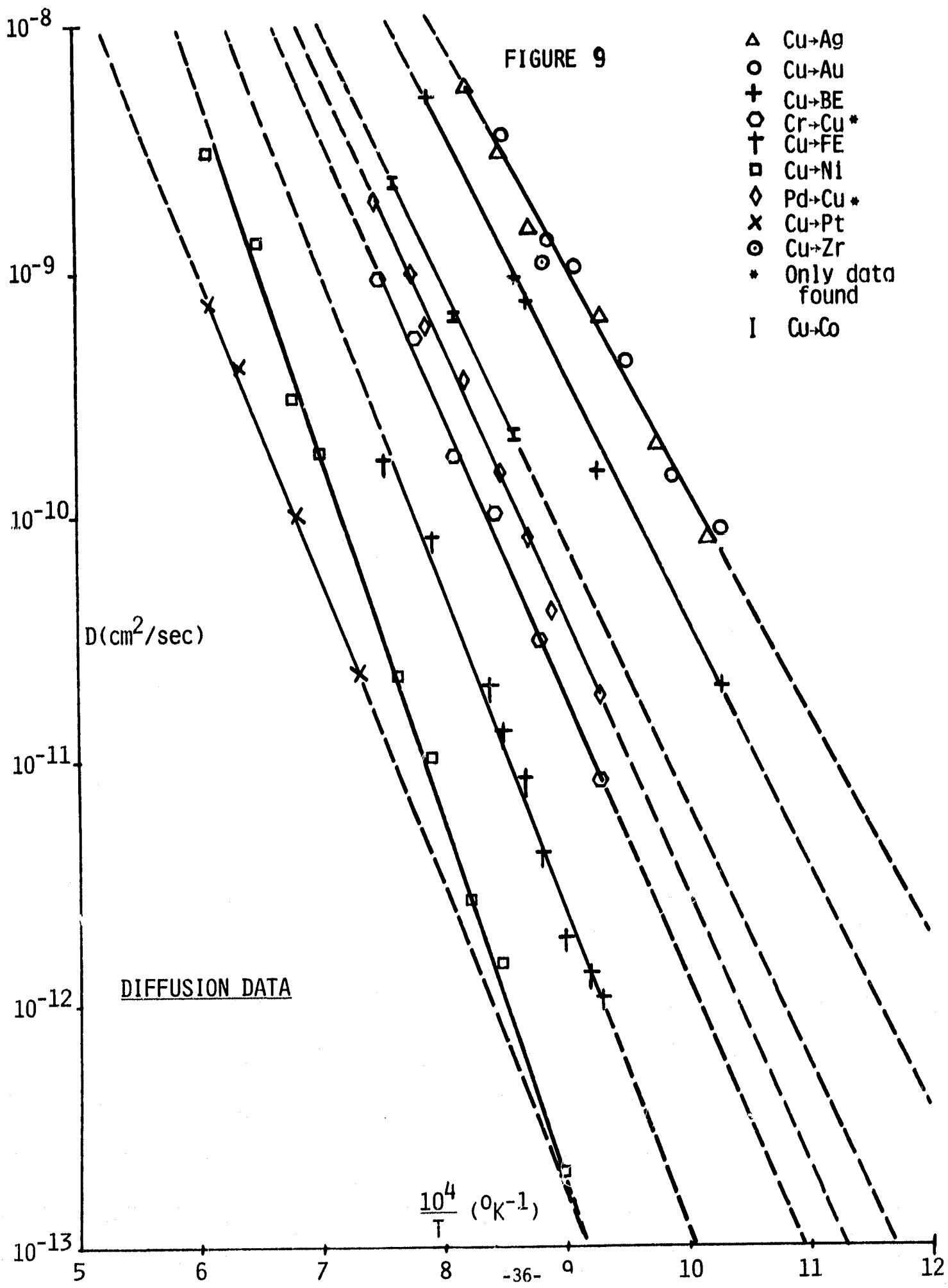
Most sources use bulk samples in polycrystalline or crystalline form. The papers used a variety of techniques of measuring copper diffusion ranging from radioactive tracer experiments to use of an electron microprobe.

Data was found on the following different metal systems: Cu \rightarrow Ag, Cu \rightarrow Au, Cu \rightarrow Fe, Cu \rightarrow Co, Cu \rightarrow Cr, Cr \rightarrow Cu, Cu \rightarrow Fe, Cu \rightarrow Li, Cu \rightarrow Ni, Cr \rightarrow Pd, Pd \rightarrow Cu, Cu \rightarrow Pt, Cu \rightarrow Sb, Si \rightarrow Ti, Cu \rightarrow U and Cu \rightarrow Zr. Also two papers were found on the Cr-Cu contact system, mainly dealing with contact stability. (See Appendix K.)

As stated in the introduction, an evaporated contact study was conducted to test the conclusions from the paper study. It is realized that plated metal layers are usually less dense than evaporated layers and that the results from the evaporation study may not apply to the plated layers.

Figure 9 shows a summary of the diffusion data found from the different sources (3). The lines on the far left of the plot are the metals that act as the best copper

FIGURE 9



barriers. The best metal appears to be platinum, with nickel a close second. Nickel was then chosen as the best candidate for a cheap platable copper barrier.

Heat Treatment Study

A heat treatment study using evaporated metals designed to test the results of the paper study was initiated and completed. The study monitored the V_{oc} , CFF and I_{sc} of active solar cells for degradation effects caused by the heating. Early experiments had shown that when copper diffuses into an active solar cell, there is an immediate decrease in the cell V_{oc} without any change in the I_{sc} (with the expected decrease also of the curve fill factor). The purpose of this study was to check experimentally if nickel is a good barrier to copper. The test matrix details are as follows:

- (i) All heat treatments were done in nitrogen only.
- (ii) Properties of the solar cells were evaluated before and after the heat treatments.
- (iii) Heat treatment details:

TIMES (MINUTES)	TEMPERATURES (°C)					
	5	400	450	500	550	600
15	400	450	500	550	600	

- (iv) Cell tests included control cells using Ti-Pd-Ag contacts.
- (v) Cell groups contained 5 cells.

Results from several contact systems were previously reported (3).

Figure 10* shows the change of the V_{oc} (of 2000 Å - thick Ag contacts) with heating, as compared to the Ti-Pd-Ag control cells. This system appears stable to about

FIGURE 10

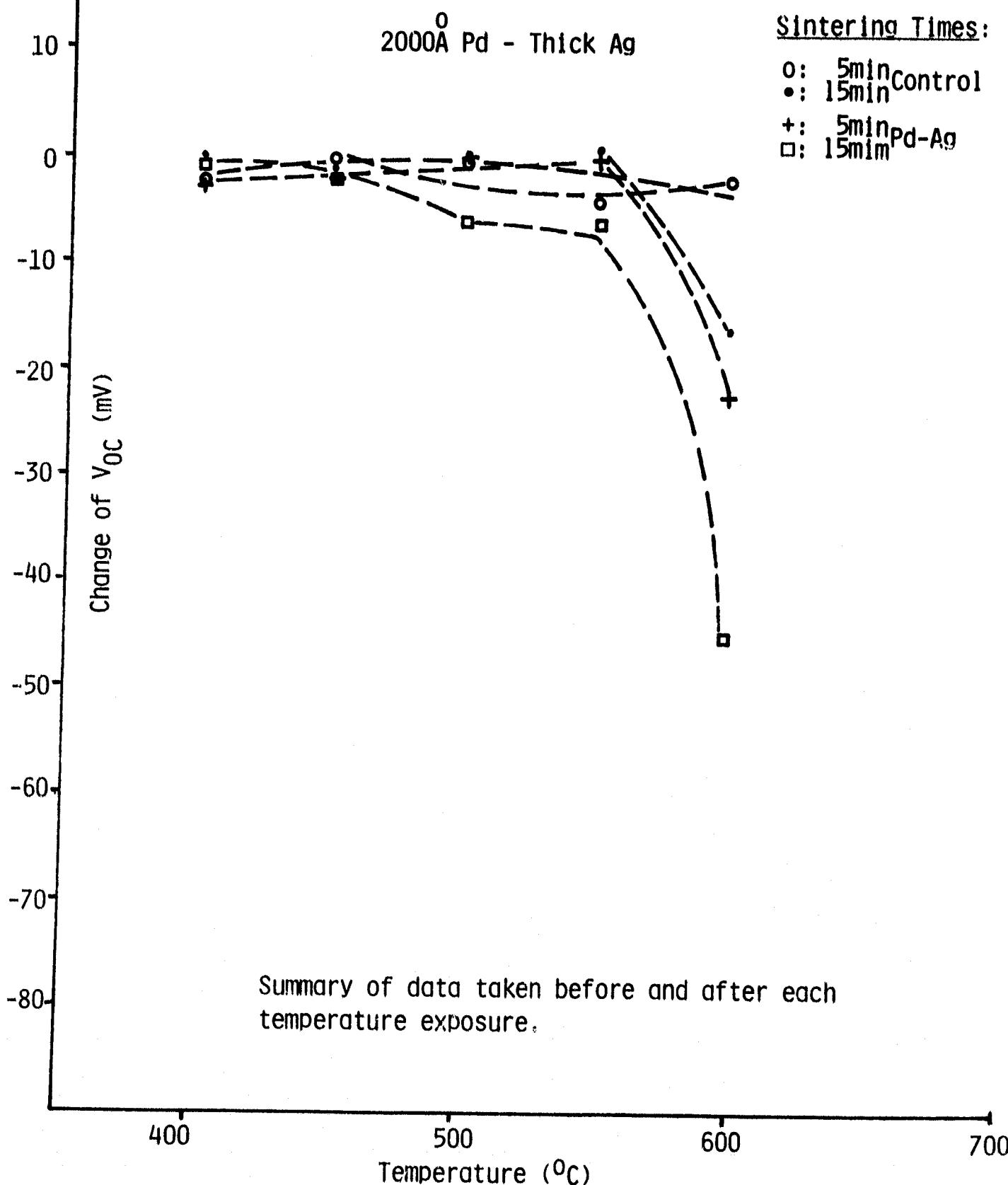


FIGURE II

2000 \AA Cr - Thick Ag

Sintering Time:

○: 5min Controls
●: 15min
+: 5min Cr-Ag
□: 15min Cr-Ag

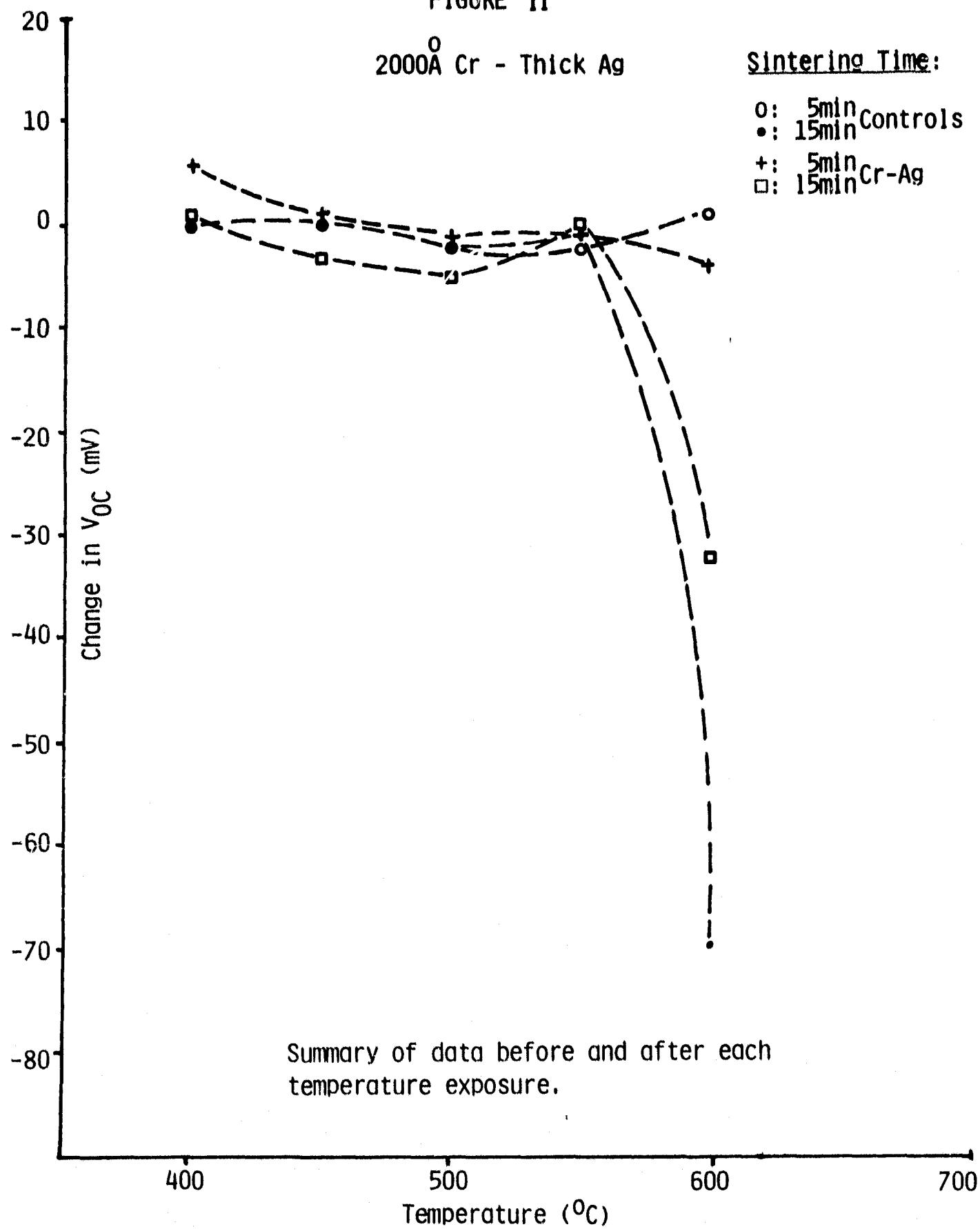
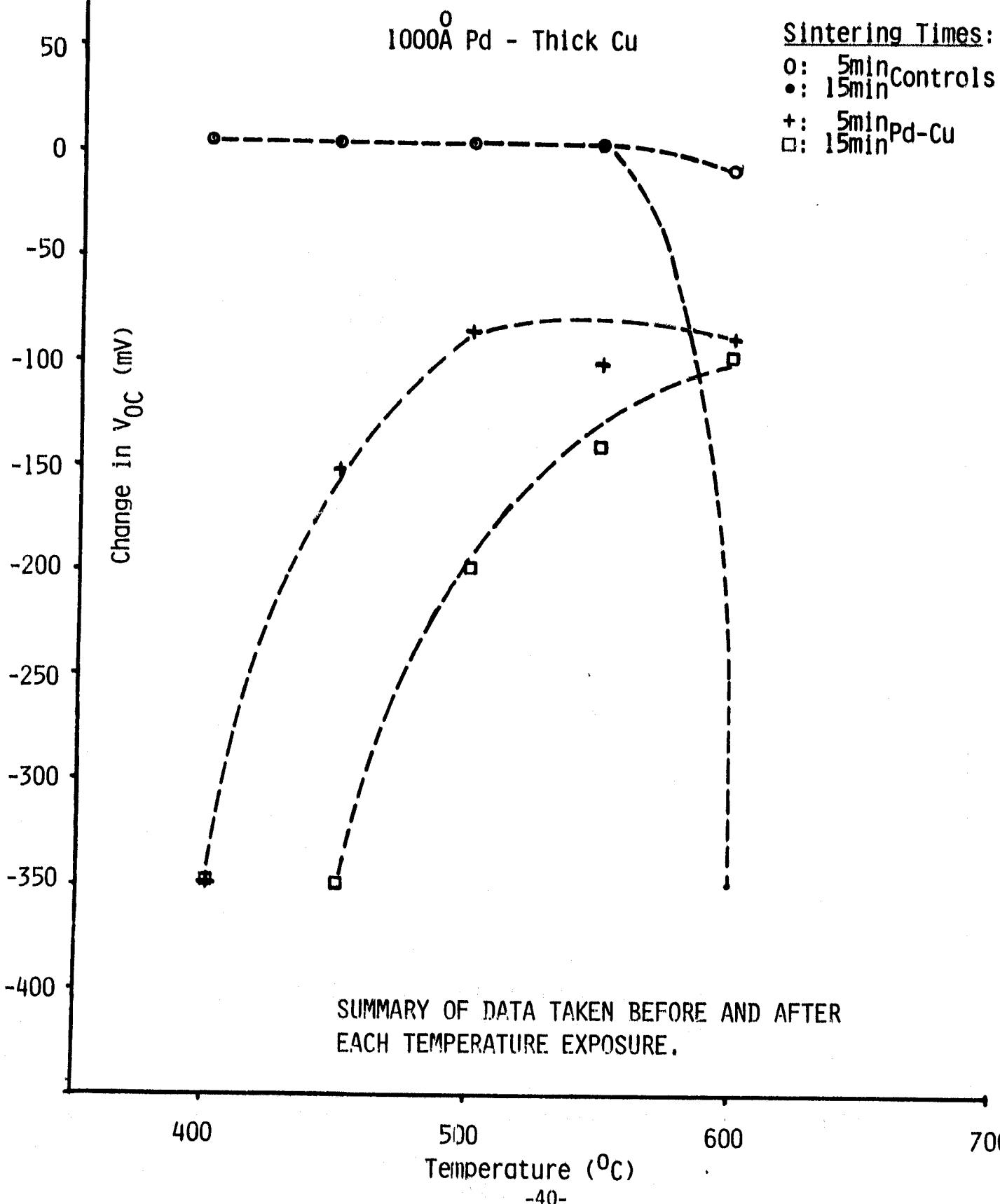


FIGURE I2



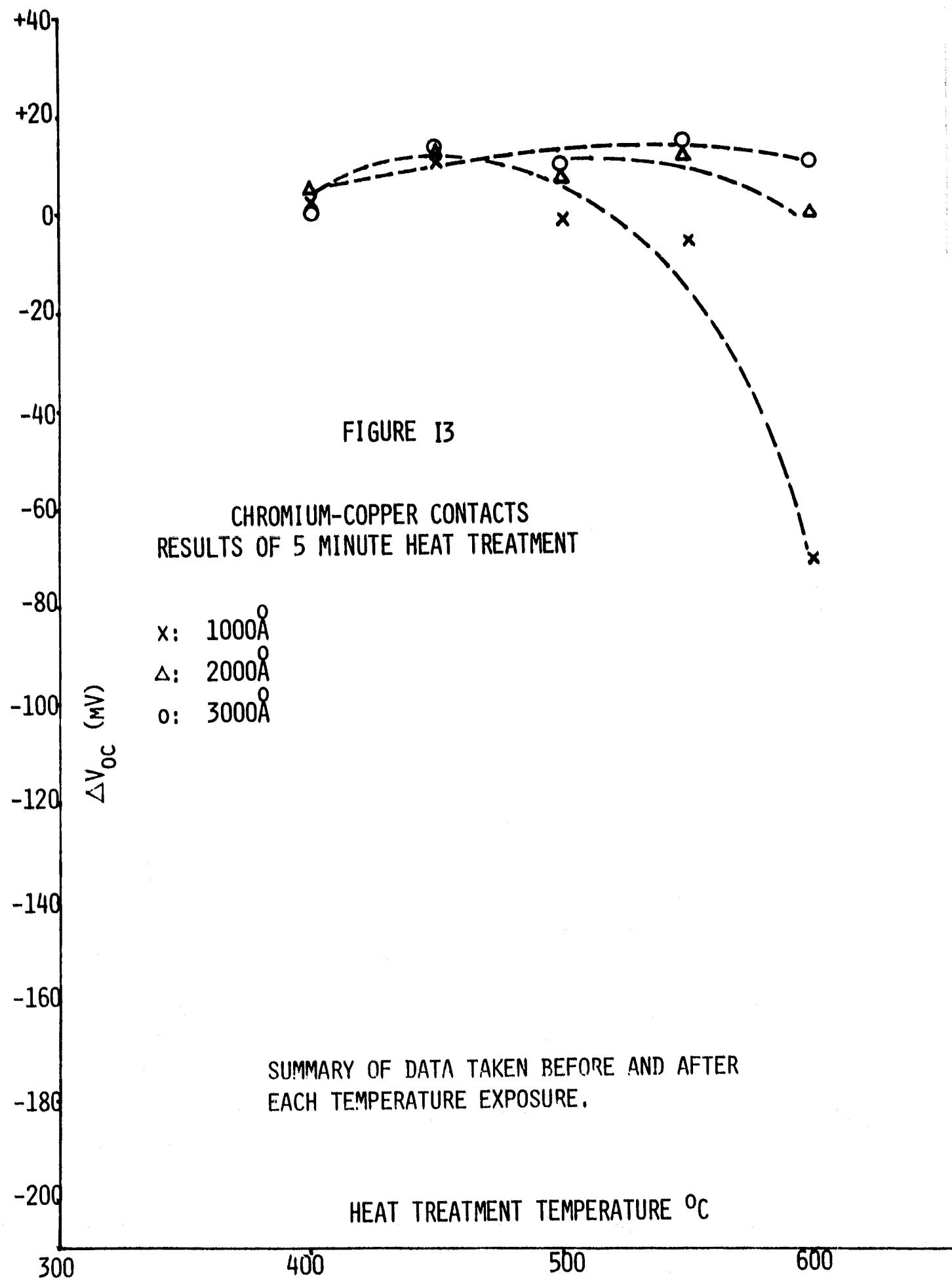


FIGURE 14

CHROMIUM-COPPER CONTACTS
RESULTS OF 5 MINUTES HEAT TREATMENTS

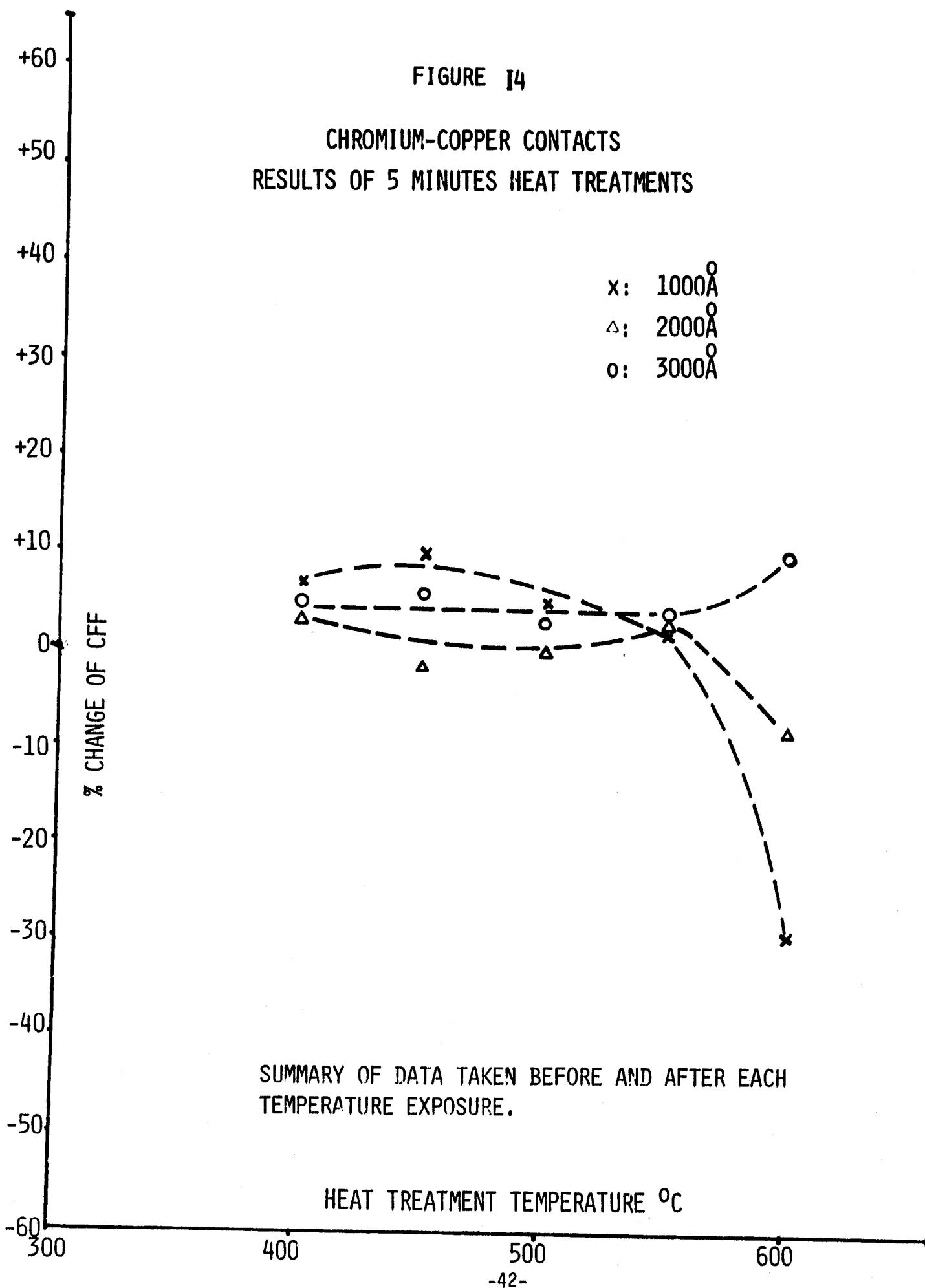


FIGURE 15

CHROMIUM-COPPER CONTACTS
RESULTS OF 5 MINUTE HEAT TREATMENT

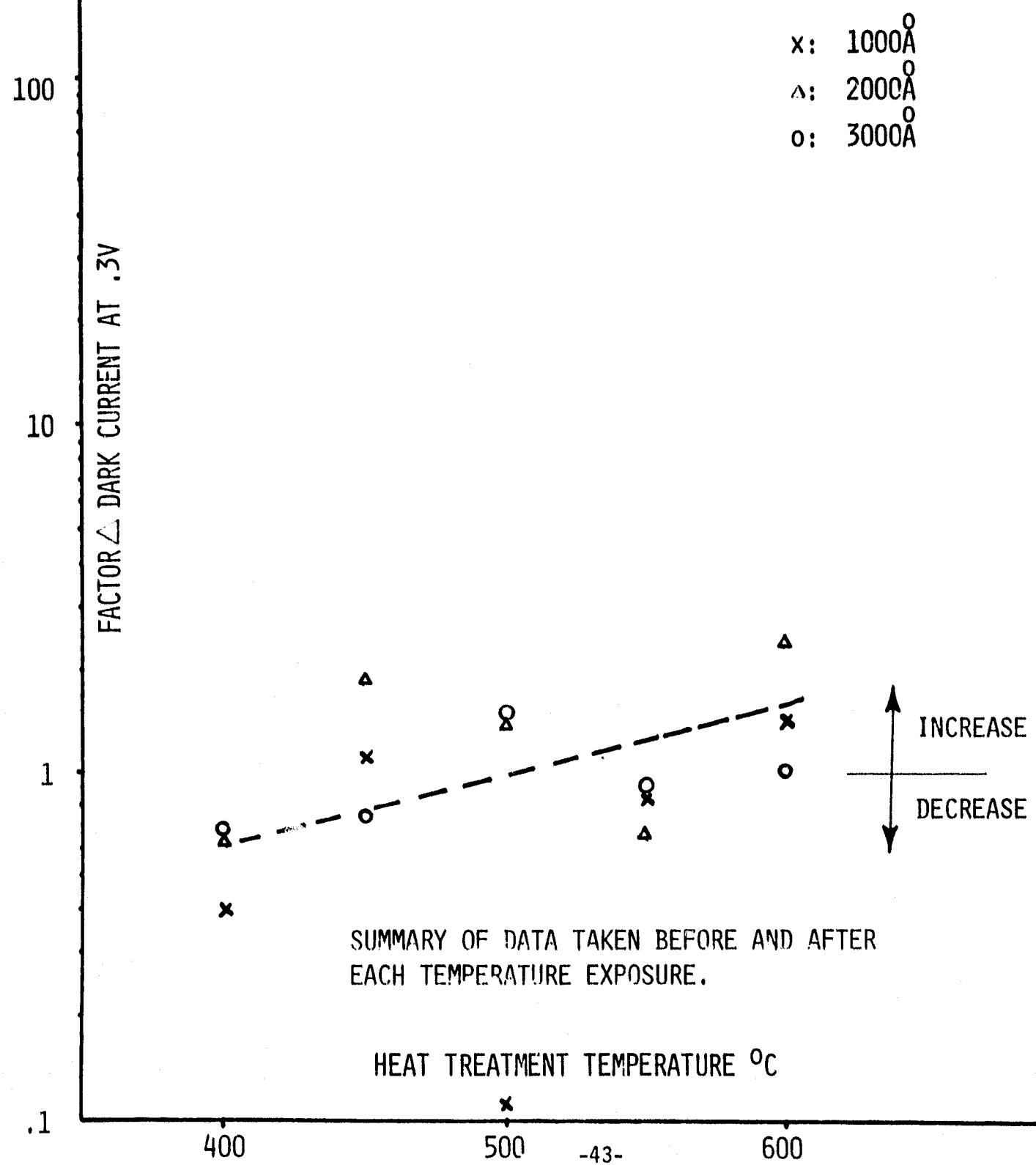


FIGURE 16
CHROMIUM-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT

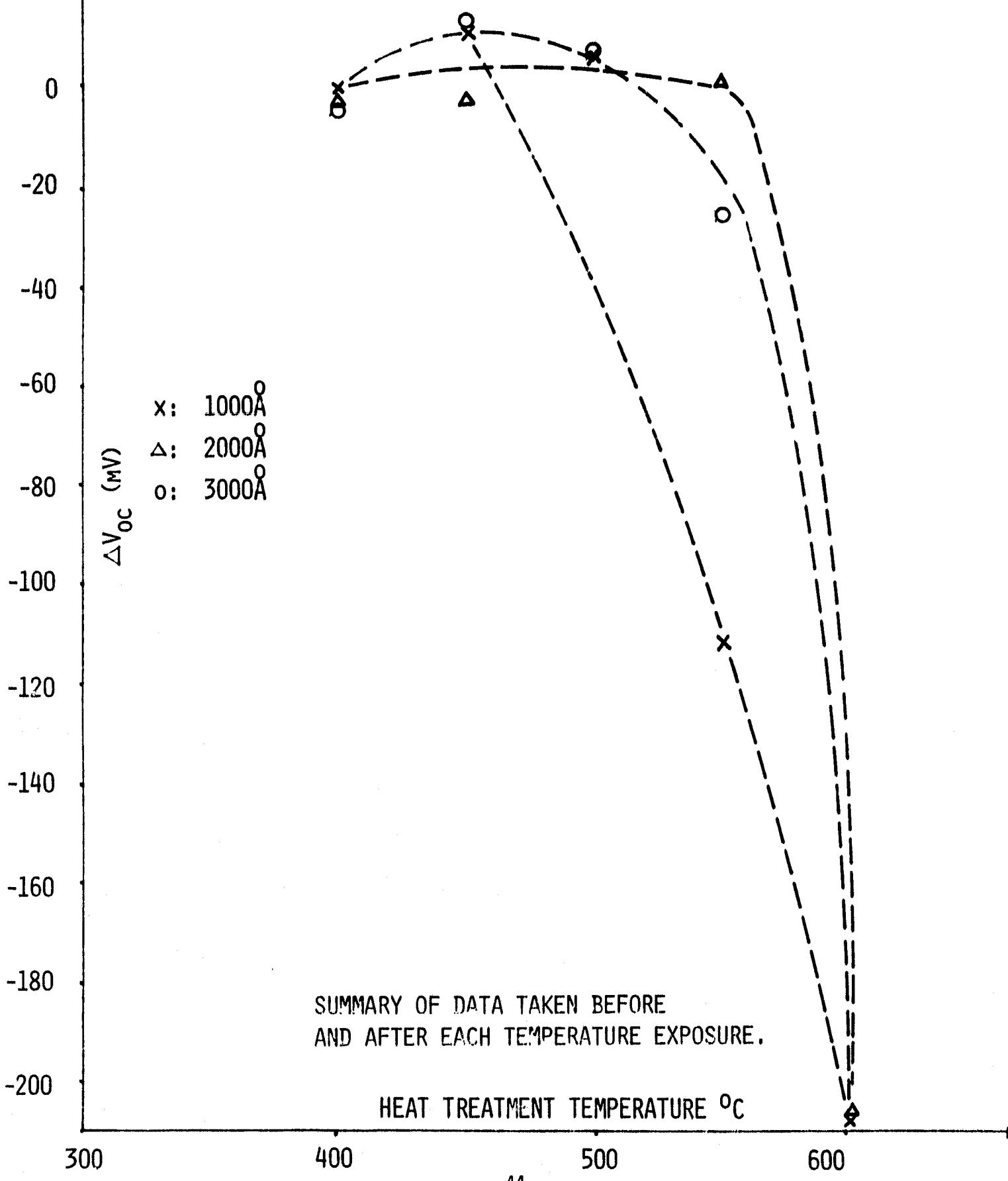


FIGURE 15

CHROMIUM-COPPER CONTACTS
RESULTS OF 5 MINUTE HEAT TREATMENT

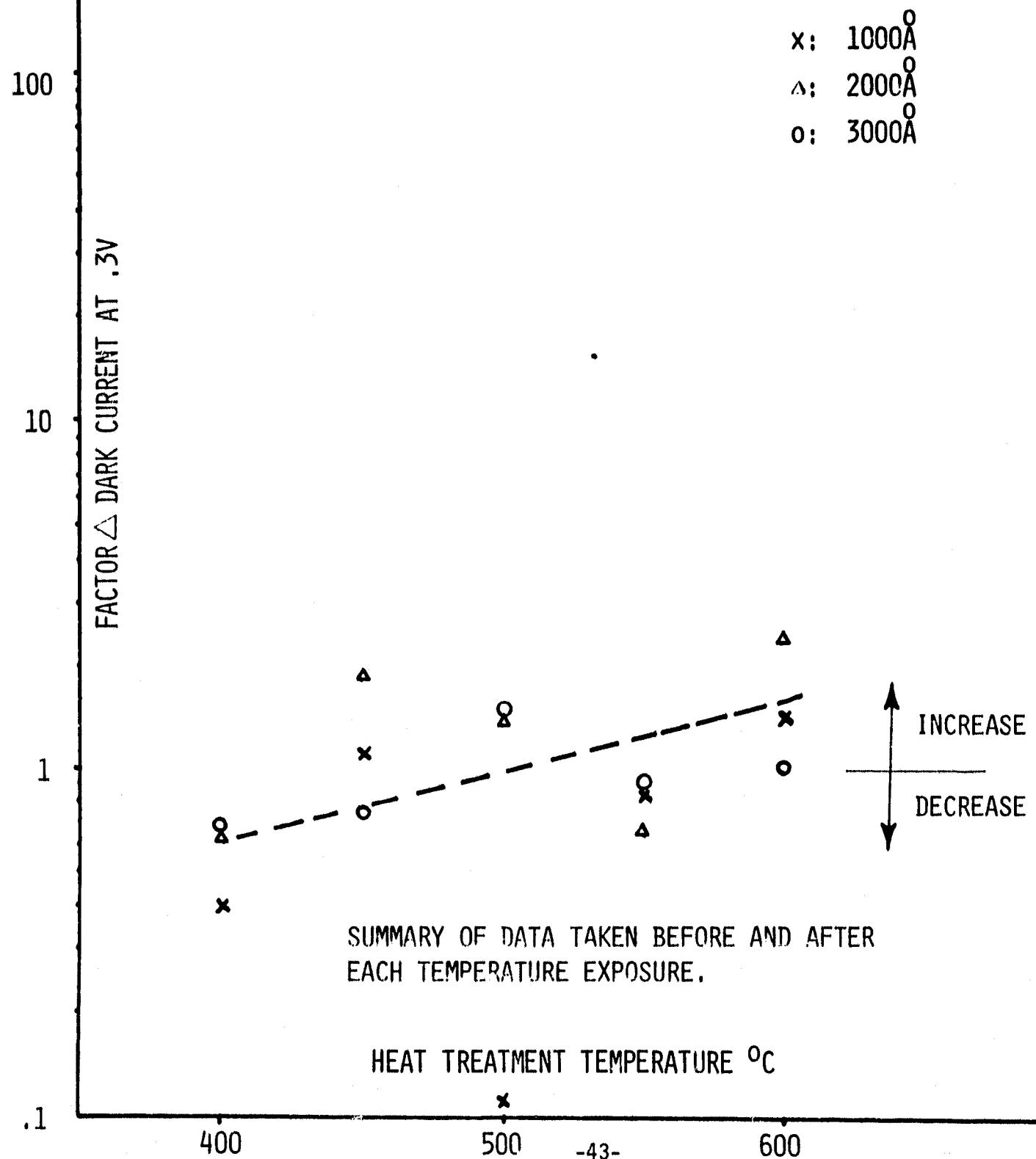


FIGURE 16
CHROMIUM-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT

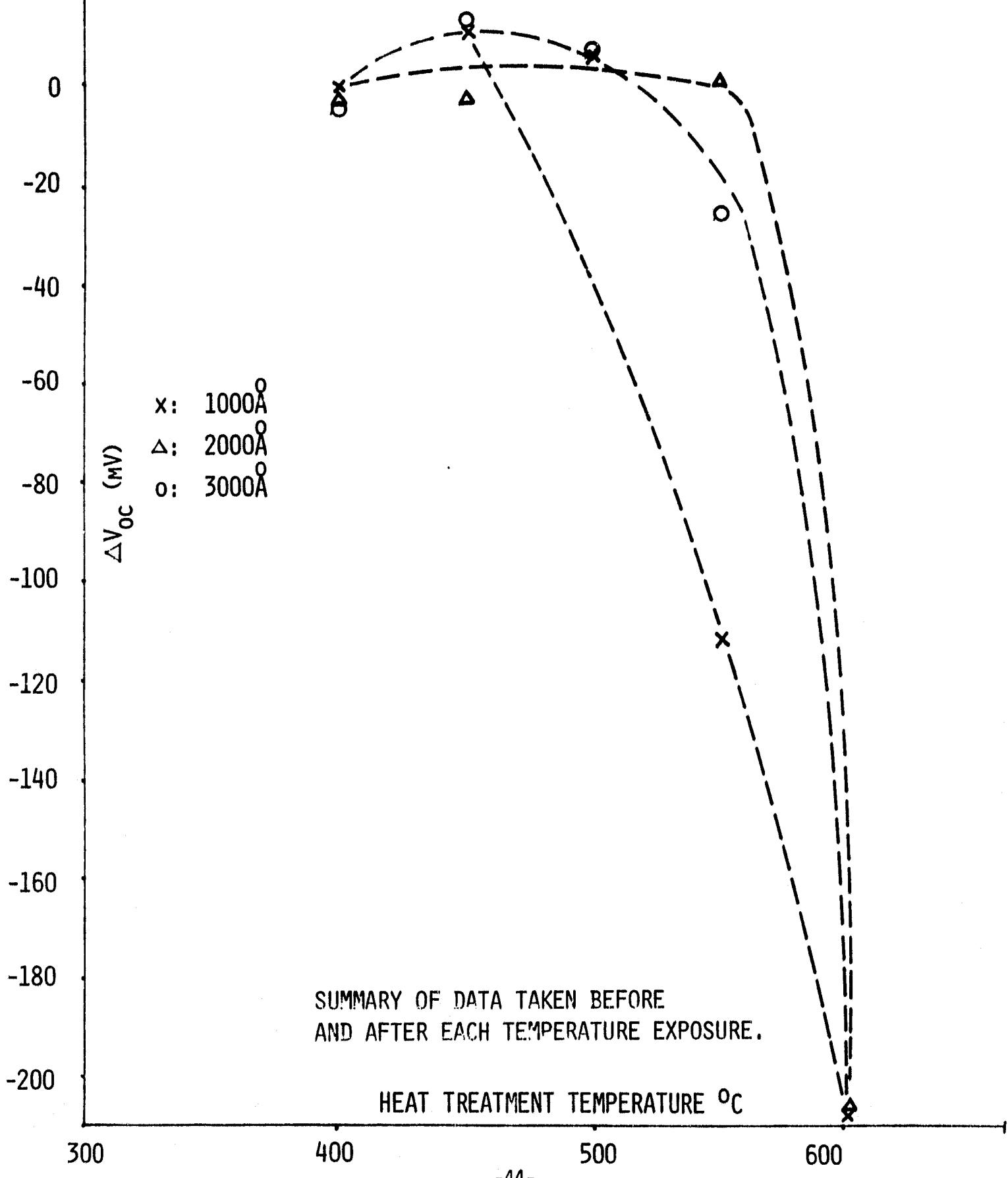
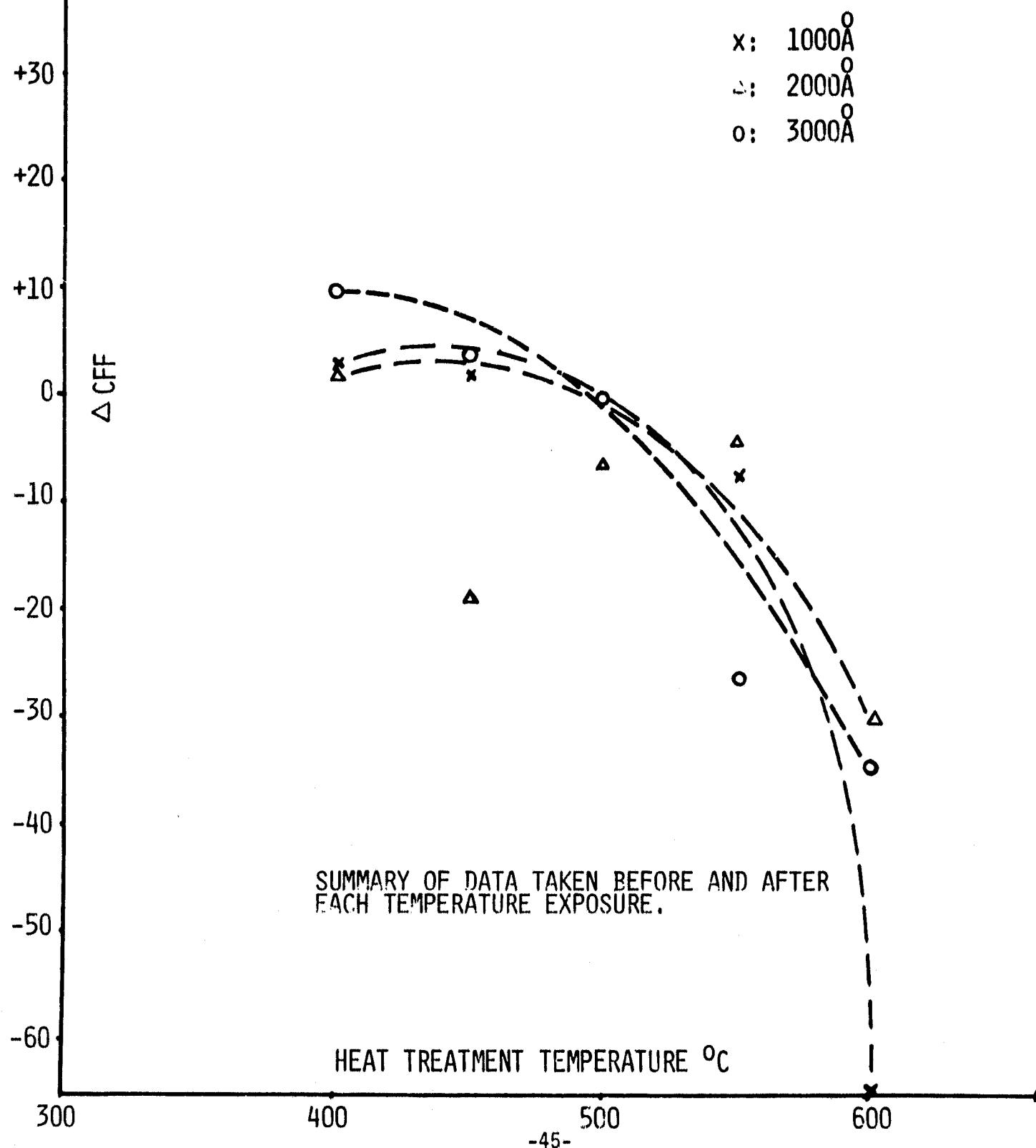


FIGURE 17

CHROMIUM-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT



1000

FIGURE 18

CHROMIUM-COPPER CONTACT

RESULTS OF 15 MINUTE HEAT TREATMENT

FACTOR Δ DARK CURRENT AT .3V

10

1

.1

SUMMARY OF DATA TAKEN BEFORE AND AFTER EACH
TEMPERATURE EXPOSURE.

HEAT TREATMENT TEMPERATURE $^{\circ}$ C

400

500

600

700

-46-

x: 1000 $^{\circ}$ A
△: 2000 $^{\circ}$ A
o: 3000 $^{\circ}$ A

INCREASE
DECREASE

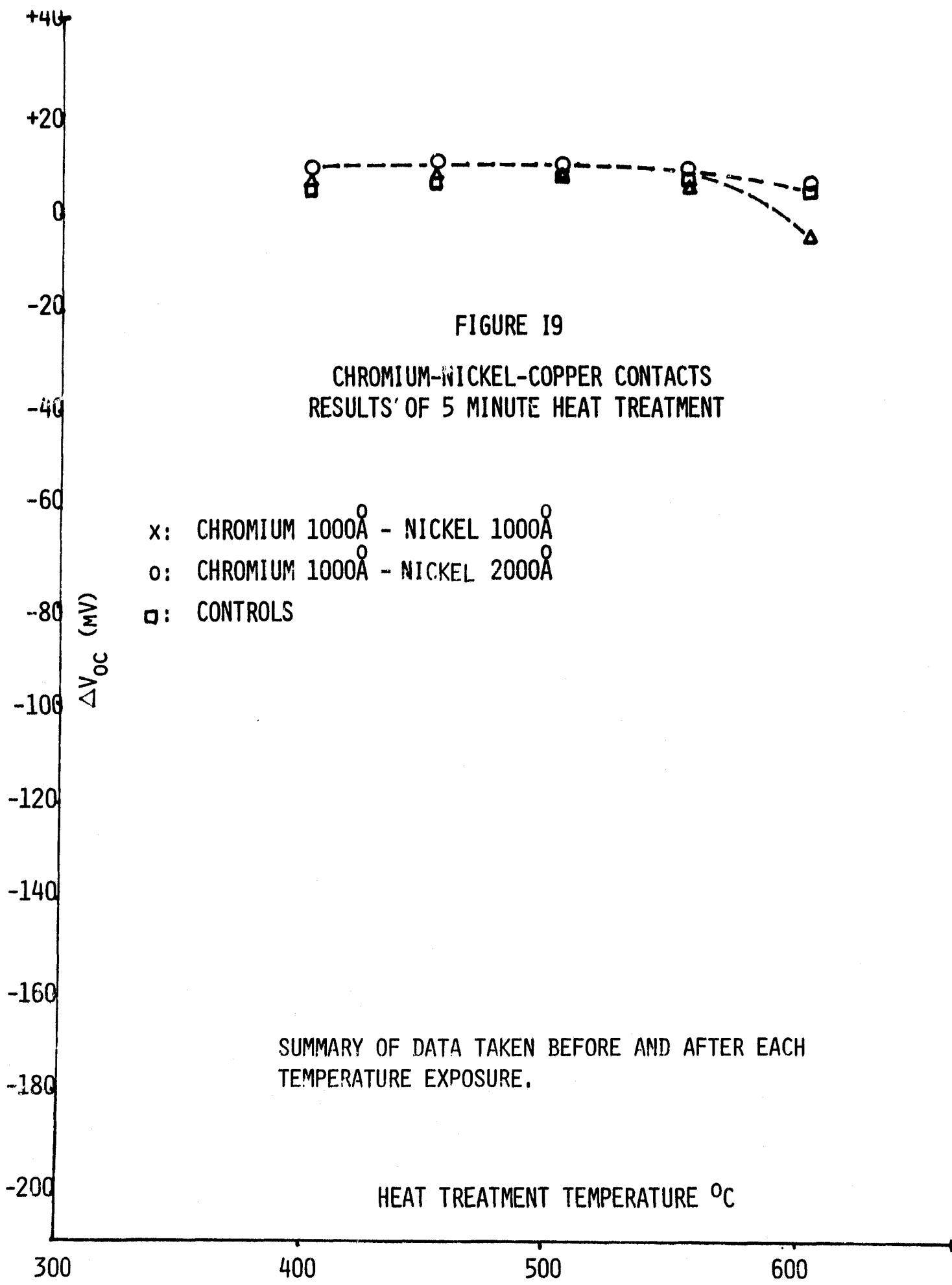
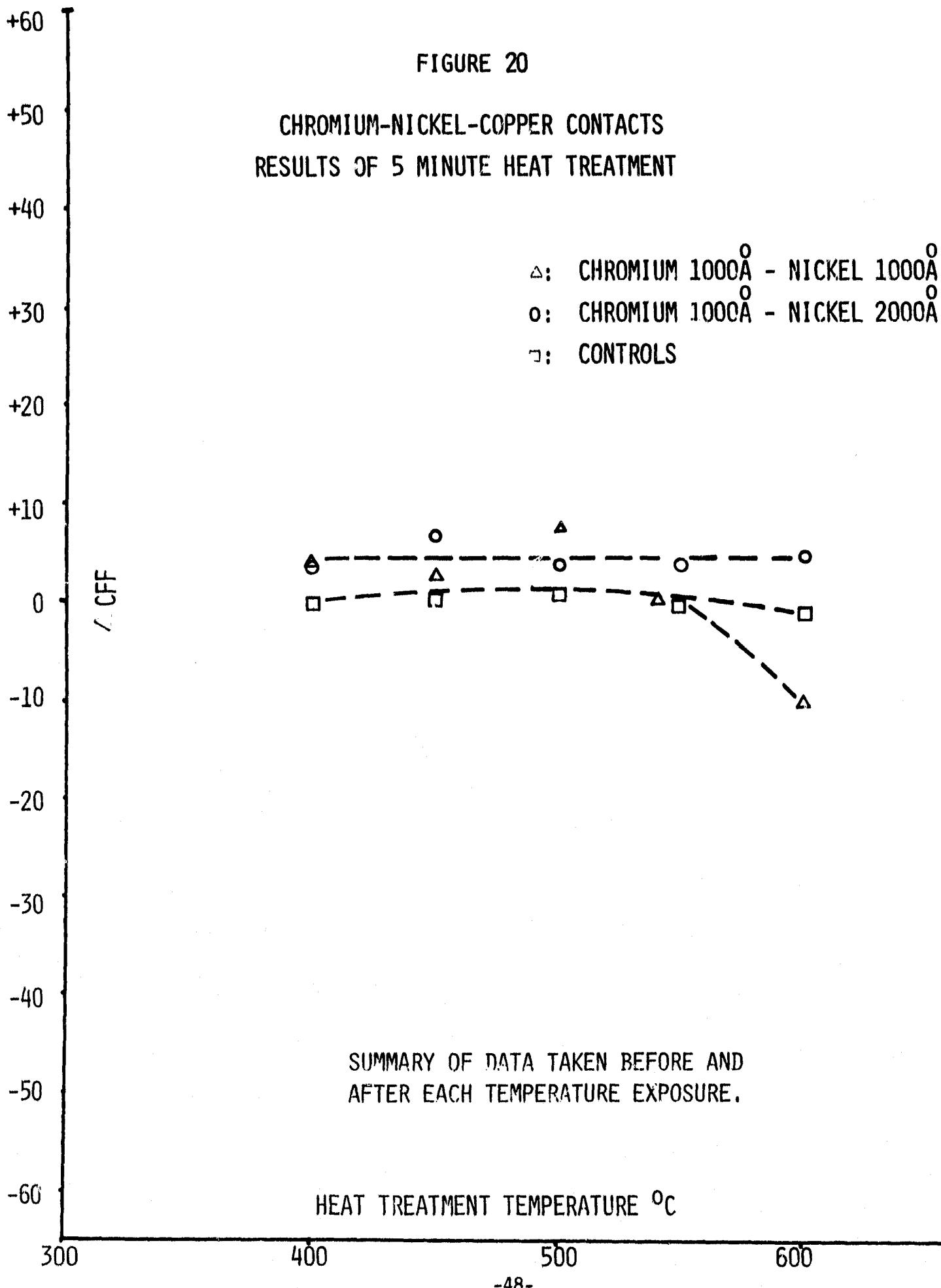


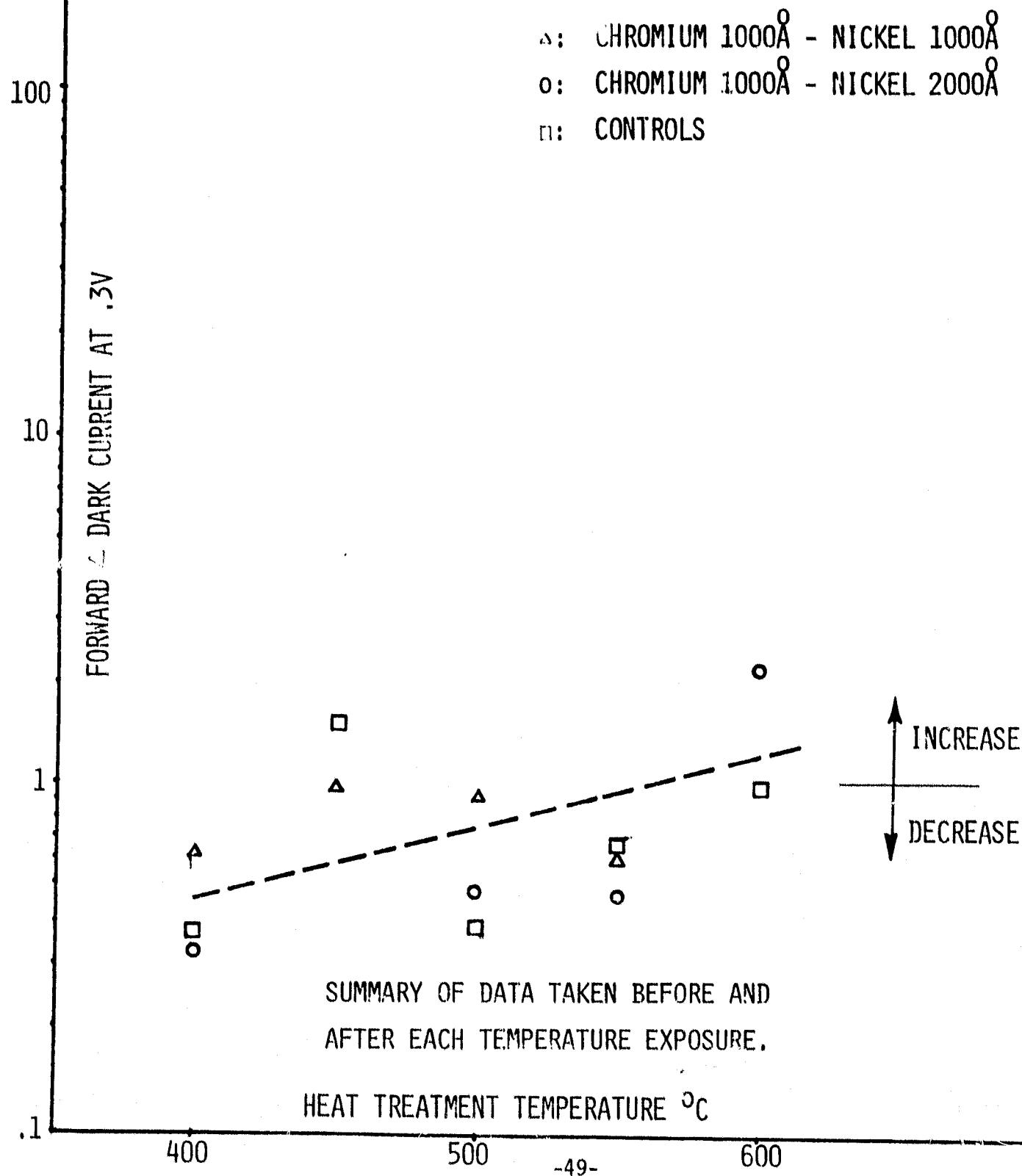
FIGURE 20
CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 5 MINUTE HEAT TREATMENT



1000

FIGURE 2I

CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 5 MINUTE HEAT TREATMENT



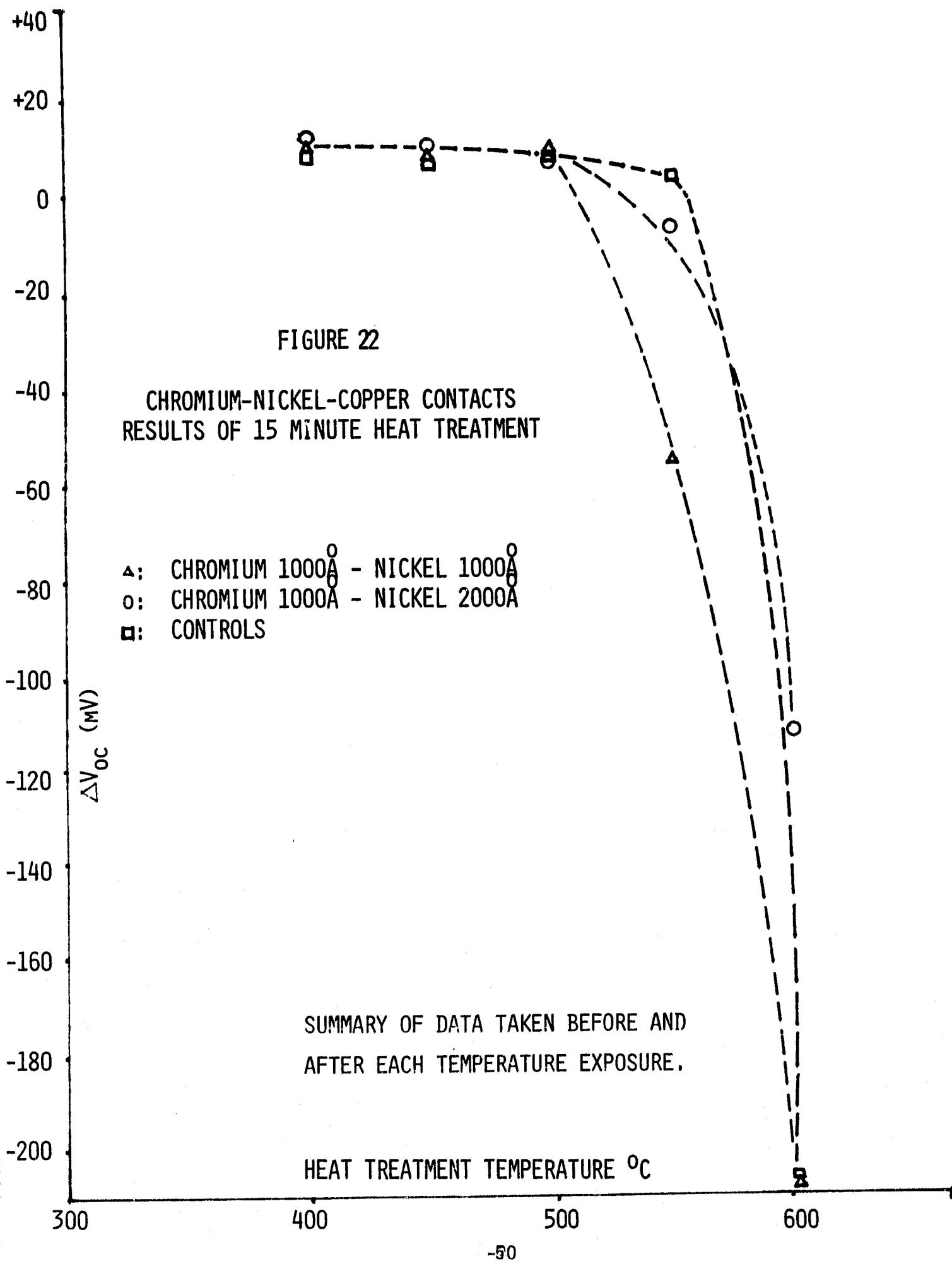


FIGURE 23
CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT

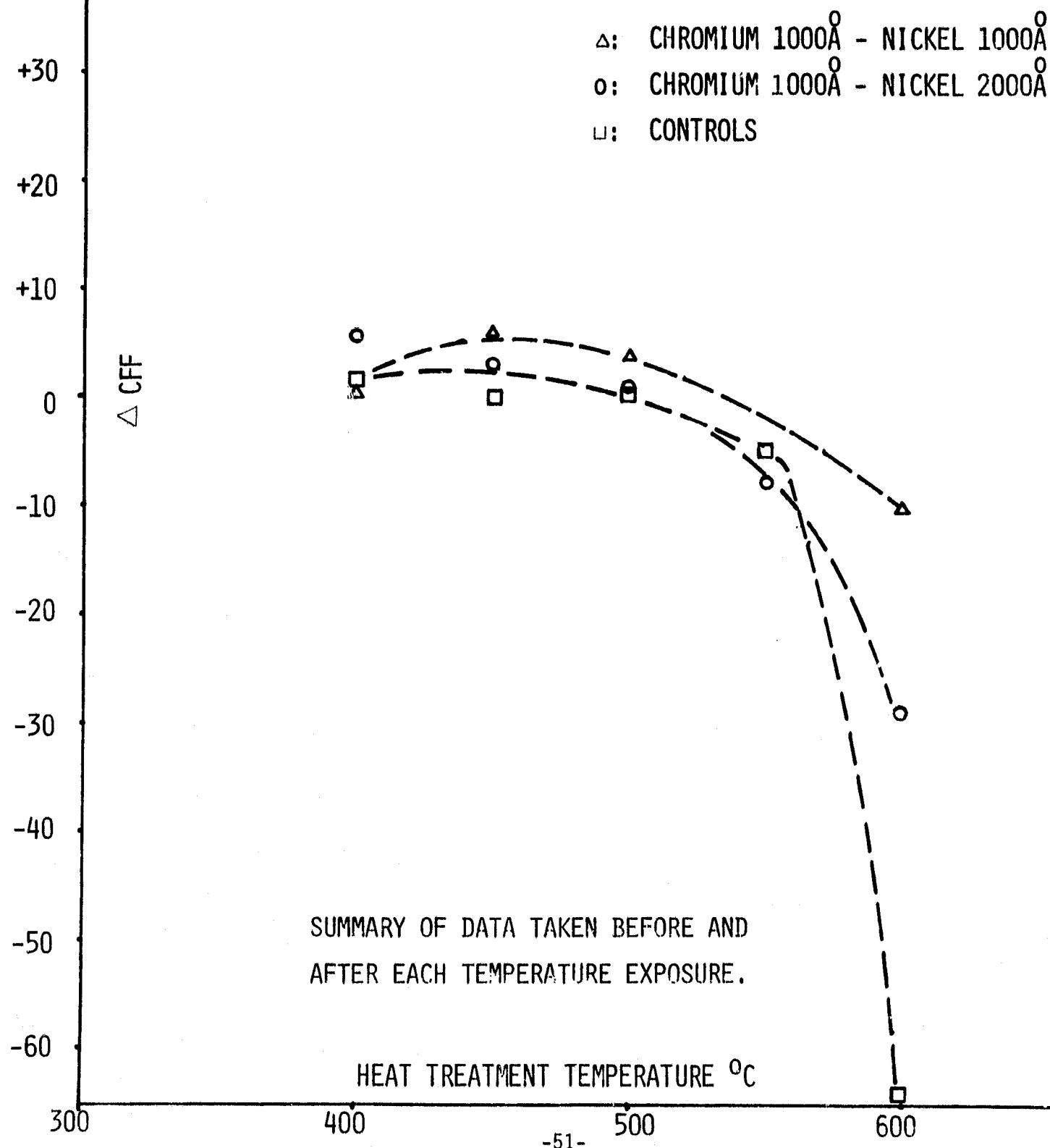
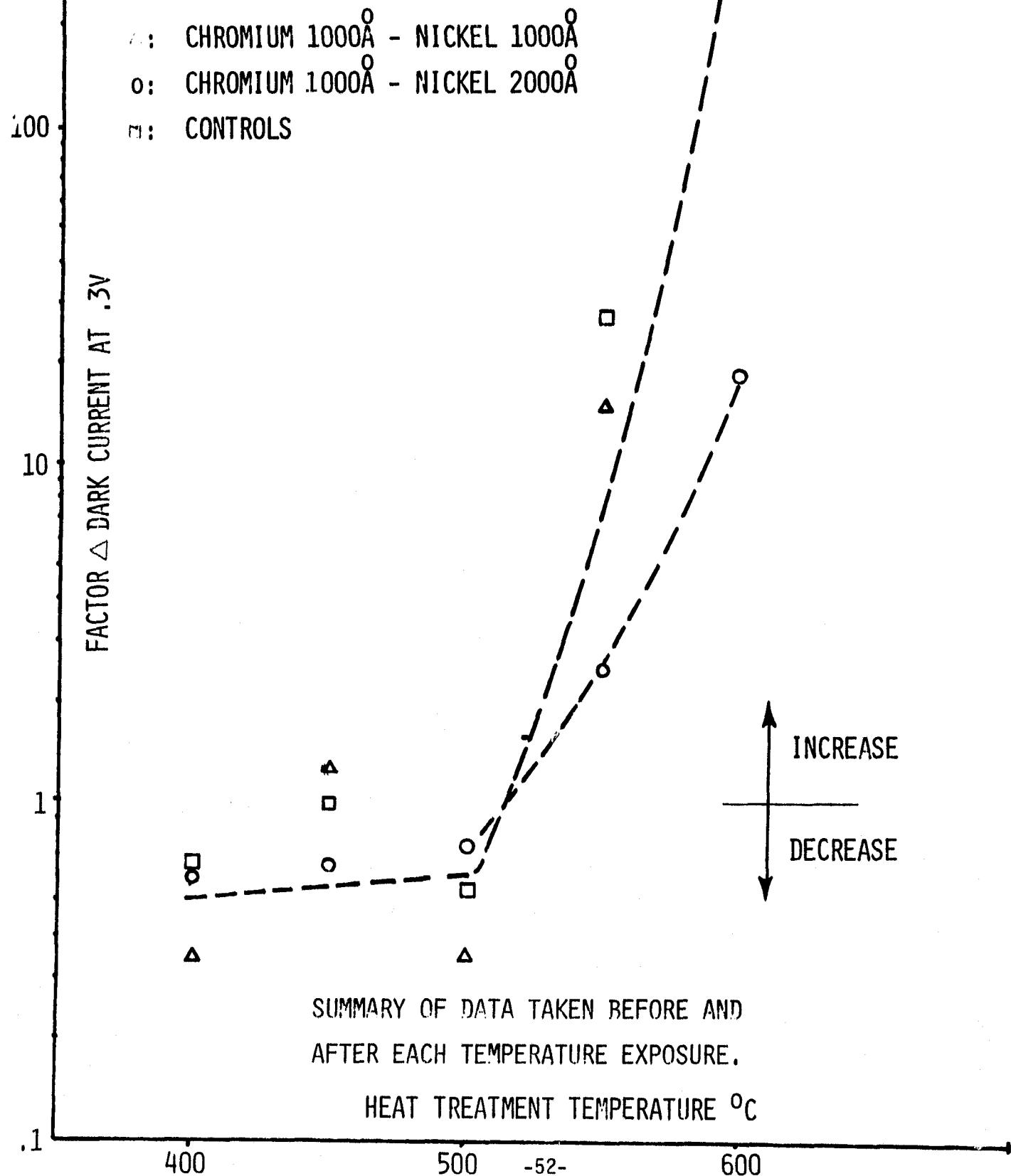


FIGURE 24

CHROMIUM-NICKEL-COPPER CONTACTS
RESULTS OF 15 MINUTE HEAT TREATMENT



500°C. Figure 11 shows the change of V_{oc} for 2000Å Cr - thick silver contacts, as compared to the Ti-Pd-Ag control cells. This system appeared stable to about 550°C. Also a test was done using 1000Å Pd and 3 microns of copper (Figure 12). The cells were severely degraded even for the 400°C heat treatment. From the paper study the diffusion data predicted that at 560°C, a 1000Å Pd layer would only protect the silicon from the copper for 51 seconds using a single mode diffusion calculation. Thus these results seem reasonable. Further experiments were not monitored and relatively no change was seen over the entire temperature range. This would indicate that if copper diffused into the silicon it did not cause any bulk lifetime reduction.

*NOTE: The points plotted on Figure 10 (and following Figure 11 through 24) represent the average measured for 5-cell groups.

For the next set of tests, more data was added to better understand the changes the devices were exhibiting during the heat treatments. The tests were expanded to measure V_{oc} and I_{sc} , the curve fill factor (CFF), and the dark forward I-V characteristics before and after the heat treatments. First chromium-copper contacts were studied using three different thicknesses of chromium, 1000Å, 2000Å, and 3000Å. Figure 13, 14, and 15 show results of five minute heat treatments. The cells with 2000 or 3000Å chromium appeared to be stable to temperatures as high as 550°C. Notice the change in CFF and in dark current at .3 volt data (Figures 14 and 15) data support the V_{oc} data (Figure 13). Figures 16, 17, and 18 show the results of the 15 minute heating for the chromium copper system. Again the 2000Å and 3000Å layers of chromium held up better than the 1000Å chromium layer cells. Perhaps the 1000Å layer cells had more pinholes or surface cracks. The 2000Å and 3000Å chromium layer cells performed well until 500°C. At higher temperatures all three plots indicated severe degradation of the cells.

The next contact system that was studied was chromium-nickel-copper. The chromium was evaporated only in a 2000\AA layer whereas the nickel was evaporated in 1000\AA and 2000\AA thicknesses. For the five minute heat treatments the contact system performed well to 550°C and only showed a small amount of degradation at 600°C . These results are shown in Figures 19, 20, and 21. Figures 22-24 show the graphical results of the 15 minute study. The cells performed better than the Ti-Pd-Ag controls at 600°C . It appears that even when the Cr-Ni-Cu Cells start to degrade (500°C) the degradation rate is slower than with the Cr-Cu cells. These results confirm that nickel is a good barrier to copper diffusion.

Experiments were also made to study the Pd-Ni-Cu system. This work would explicitly show the barrier qualities of nickel, since palladium is such a poor barrier. Palladium (if it is not sintered) does not stick to the silicon surface very well and when the highly stressed nickel layer was deposited the contacts lifted off. Therefore, no reasonable results were obtained for Pd-Ni-Cu contacts.

Plating Mask

In the present process, two plating masks are used for different steps in the process. The first mask (mask A) establishes the contact pattern (by etching) in the second mask (mask B) and protects this mask from the immersion palladium bath. The second mask (SiO_2) shields the large non-contacted areas of the cell from the other plating baths (since the mask A is removed after the immersion palladium plating). Also this mask restricts the copper plating to the previously metallized areas and minimizes copper contamination of the silicon surface.

In phase I, mask A was a photoresist mask. This was known to be expensive and work was done in Phase II to find a less costly mask. The newly developed mask A was a screen printable plastic plating resist which was solvent removable. Figures 25 and 26

shows the contact pattern developed for the 2½" diameter cell with a typical I-V Plot, and Figure 26 and 27 shows the pattern used for the 3" diameter cells with a typical I-V plot also. Both patterns yielded line resolutions of about five mils and contact coverages of 10 to 12%.

Mask B throughout the program was a CVD deposited SiO_2 layer. This layer once patterned (using Mask A) performed very well in all other baths except the immersion palladium bath. Table 9 shows the results using a number of different plating masks. On this table the masks are evaluated in all the different baths.

At the end of Phase II we were left with the conclusion that nickel was the best barrier material and it should be incorporated into the process. This would be included in old system: (a) immersion palladium bath (b) chromium bath (c) nickel bath (d) electroless copper bath (e) electrolytic copper and (f) corrosion barrier layer. This process seemingly was getting more complex and certainly more expensive. Therefore, work was done on simplify the process, but including the nickel barrier layer.

Phase III

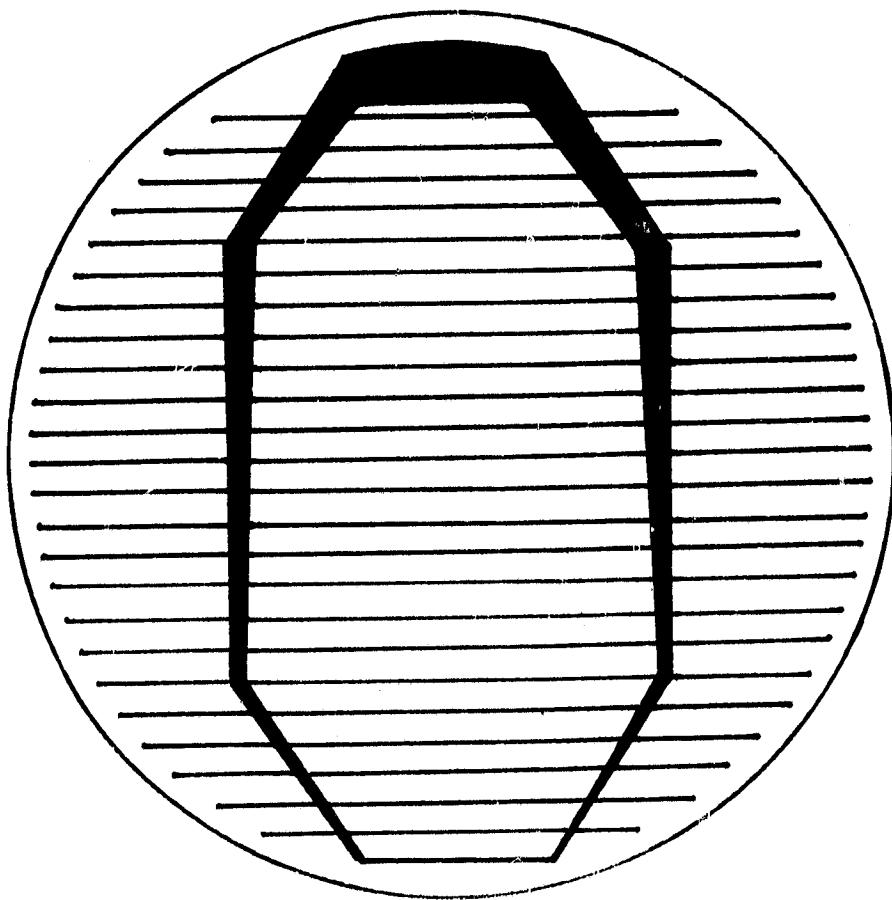
Work was done on (a) effort to replace the immersion palladium bath with an adherent nickel bath (b) replace the chromium layer with a single nickel layer and (c) elimination of the electroless copper layer and using just the electrolytic copper layer.

Palladium Bath Replacement

It was hoped that an "immersion nickel bath" might be found that would yield the same results obtained by the immersion Pd bath, that is, a low contact resistance, highly adherent layer. Since palladium also is the only "noble" metal used in the process, its replacement might yield a process requiring only one sintering.

FIGURE 25

2 1/4" Diameter Contact Pattern



Contact Coverage: 12%

Grid Line Thickness: <5 mil

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FIGURE 26

Plated Pd-Cr-Cu Solar Cell With Print-On Plating Mask .

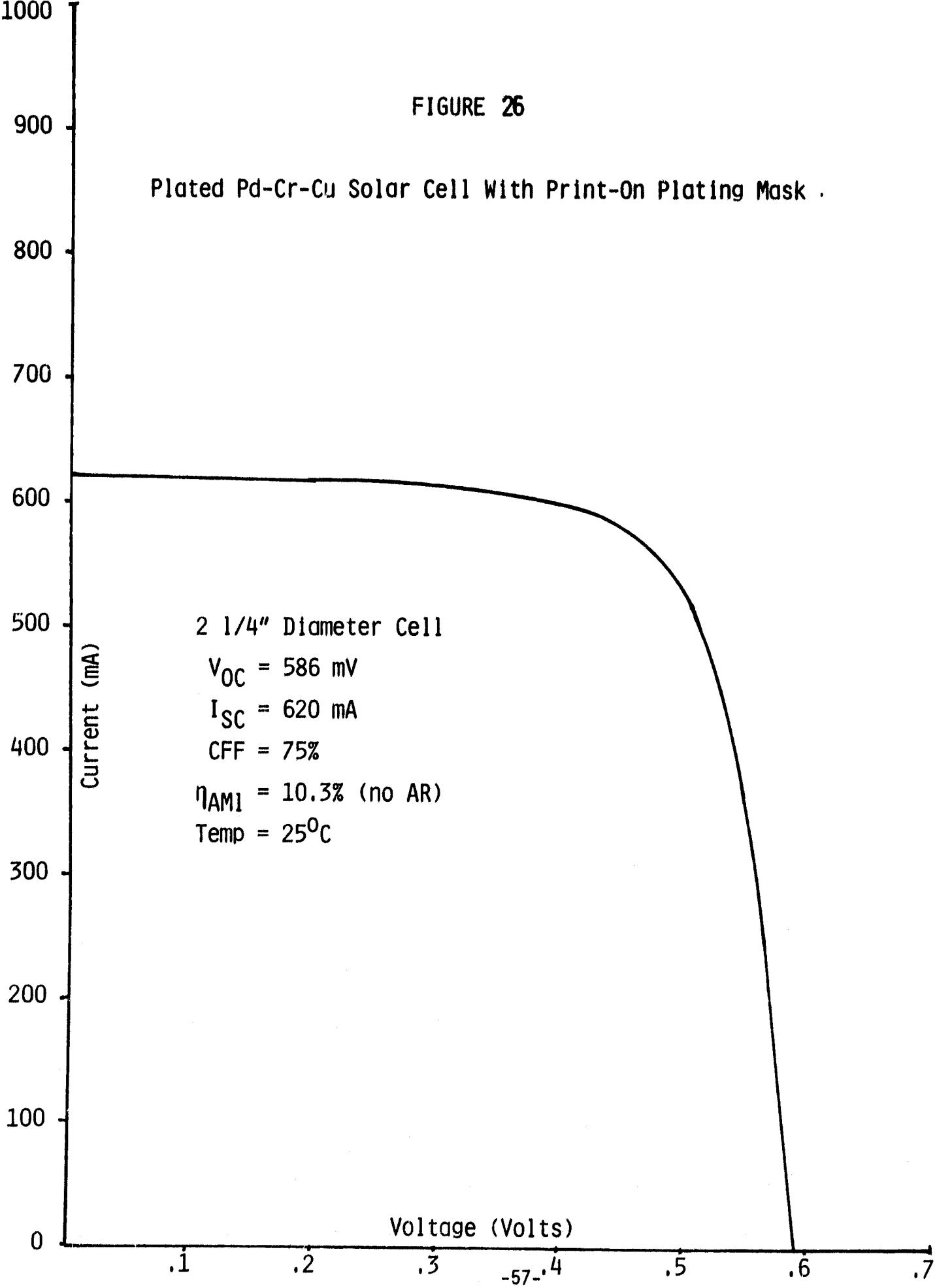
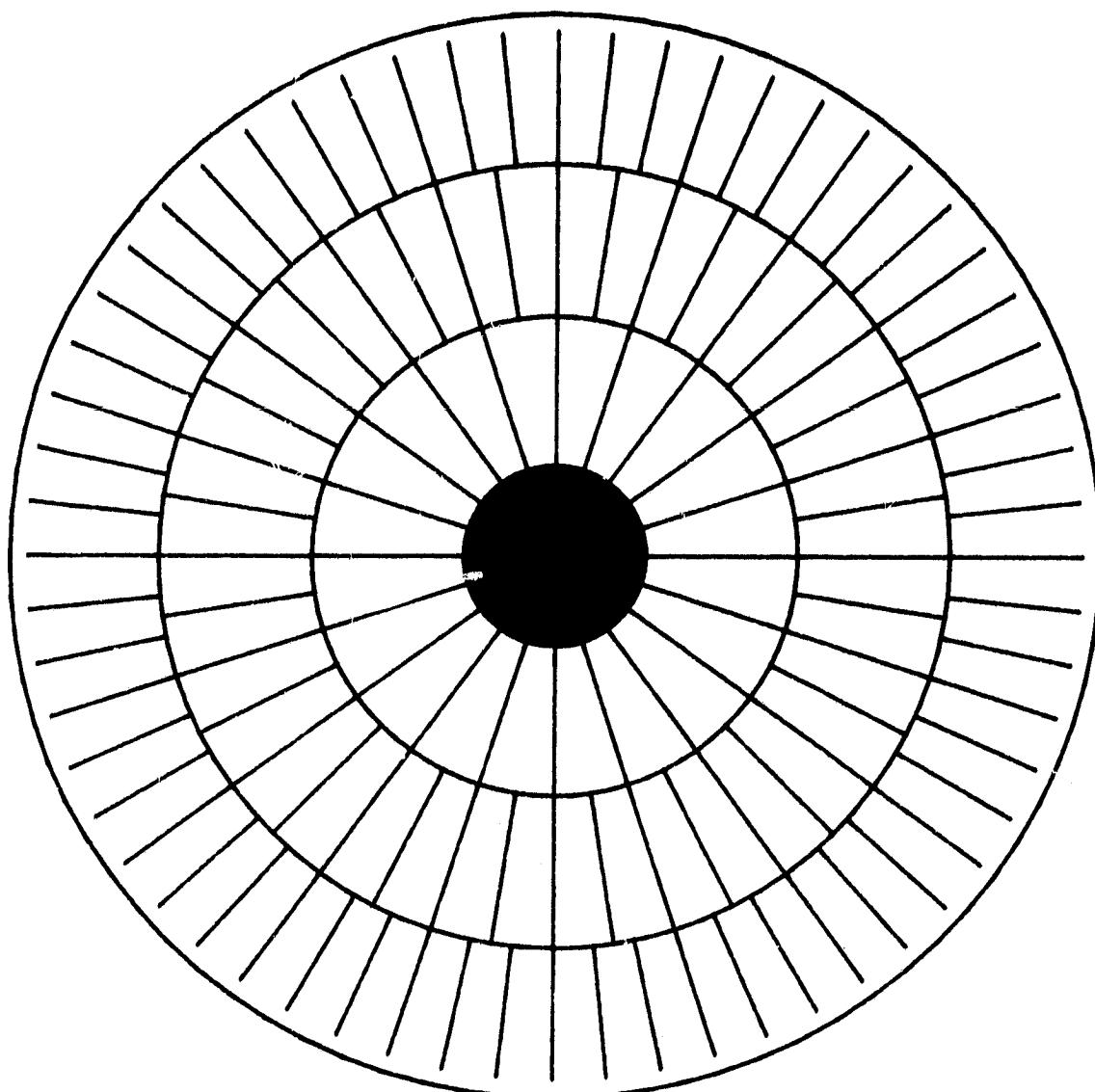


Figure 27



CONTACT COVERAGE 10%

GRID LINE WIDTH 5miles

FIGURE 28

APPLIED SOLAR ENERGY CORPORATION

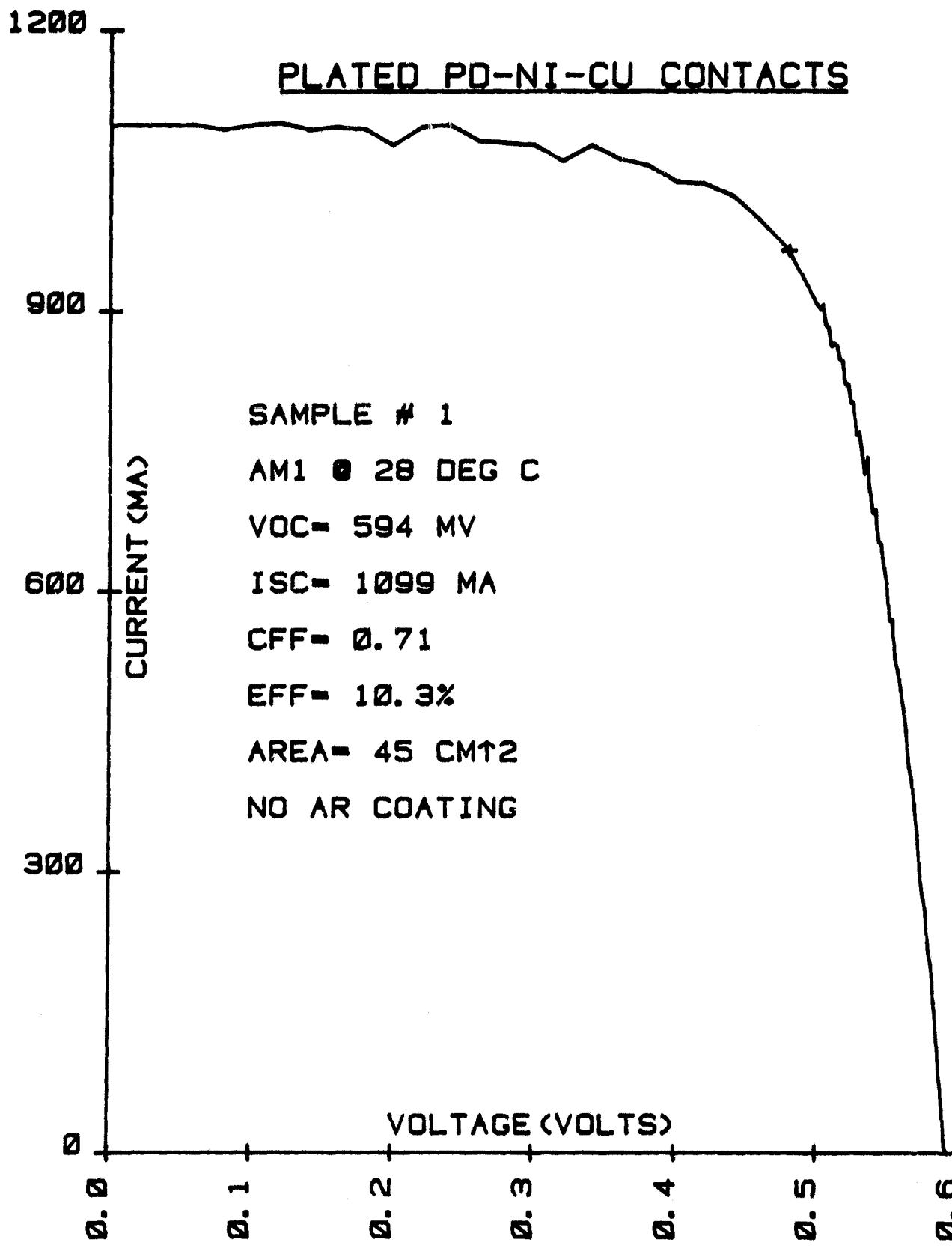


TABLE 9

PLATING MASK RESULTS

PLATING MASK	RESULTS	BATH TYPE	FAILURE REASON
POSITIVE PHOTORESIST	3	A	Became brittle with heat Desolved
	2	B	
	0	C	
CVD - SiO ₂	0	A	Etched
	3	B	
	3	C	
SiO - EVAPORATED	0	A	Etched and plated palladium
	3	B	
	3	C	
Ta ₂ O ₅ - EVAPORATED	0	A	Plated palladium every- where
	3	b	
	3	C	
Si ₃ N ₄ - LOW TEMP.CVD	2	A	Slightly etched
	3	B	
	3	C	
PRINT-ON MASK	3	A	Became brittle with heat
	2	B	
	3	C	

NOTES: 0-poor, 1-fair, 2-good, and 3-excellent.

Masks are rated only in their ability to hold up to
the plating solutions.

Baths: A - Immersion Palladium
B - Chromium Bath/Nickel Bath
C - Electroless Copper

The first bath tested was a "basic" bath activated by a boron compound instead of a phosphorus compound. The resultant plated nickel should contain no phosphorus and only 2% boron. The solution was mixed as follows:

- 1) Nickel Sulfate - 20 gm/l
- 2) Potassium Sodium Tartrate - 40 gm/l
- 3) Sodium Borohydride - 23 gm/l
- 4) Ph (adjust with NAOH) - 12.5
- 5) Temperature 40-45°C

The solution was found to be very unstable and if the Ph fell below the 12.5, the bath would quickly decompose. The plated layers of nickel even using different heat treatments were not very adherent, results which made the bath less attractive.

The second nickel bath tested was an acidic bath Ph 5-5.2. The formulation of the bath is as follows:

- 1) Nickel Sulfate - 80 gm/l
- 2) Sodium Acetate - 12 gm/l
- 3) Boric Acid - 8 gm/l
- 4) Ammonium Chloride - 6 gm/l
- 5) Sodium Hypophosphite - 24 gm/l
- 6) Temperature - 93°C

This bath, though very stable, would not plate nickel unless the surface of the cell was sensitized with palladium, therefore, rendering the bath useless as a palladium bath replacement. There were other baths that could be tried, but they were beyond the scope of the present contract. The summary remarks on nickel plating are that nickel could not be plated satisfactorily onto silicon surfaces. Hopefully, work can be continued in the search for a bath replacement.

Chromium Bath Replacement

With the addition of the necessary nickel layer to prevent copper migration, the contact process was getting too lengthy and complex for a low cost process. It was thought that the chromium layer from the old process could be wholly replaced by the nickel layer instead of adding the additional nickel layer to the old process. This certainly will be a more cost effective route in achieving a low cost contact system.

Removal of The Electroless Copper Step

It was found if the electrolytic copper was plated to the nickel layer at a very slow initial rate, good adhesion was obtained. This eliminates the need for the electroless copper layer, which is another cost savings.

Final Plating System

The final plating process first used the immersion palladium bath (50A) for 5 minutes followed by a sintering at 400°C for 10 minutes in nitrogen. The loose palladium material is removed by a 2 second aqua regia dip followed by a 5 minute DI water rinse. Next a 6 minute electroless nickel plating (2000\AA) is done followed by an electrolytic copper plating (5 microns). Last, the cells are sintered for 5 minutes at 300°C in nitrogen. This step not only improves adhesion, but also "weeds out" any defective cells with copper diffusion problems (pinholes in the nickel layer). The problem with this process has only appeared in 1-2% of the cells.

Sintering Study of the Final Plating Sequence

For proper evaluation of the plated contact system, a test heating matrix was set-up to evaluate the finished plated cells for resistance to copper migration. The earlier system, that used Pd-Cr-Cu contacts showed copper degradation with sinterings as low as 300°C for 5 minutes in nitrogen. Table 10 shows the results of the sintering test

using 2 $\frac{1}{2}$ " diameter cells and the Pd-Ni-Cu contact system. Each data point, an average of three cells, relates the change of open circuit voltage V_{oc} , the short circuit current I_{sc} , and the curve fill factor CFF. The plus or minus signs relate a positive or negative increase or decrease. Notice in Table 10 that with the 400°C 15 minute sintering, the cells show severe shunting, characteristic of copper diffusion. Therefore, our new contact system will tolerate 100°C more in temperature before copper migration shunts the cell (400°C for 5 minutes). More work in the future should be done on relating these time temperature tests to actual in the field studies. (Panels will be constructed with these cells and taken through laboratory environmental studies as well as field exposure studies for a full evaluation.)

Contact Pull Tests of the Final Plating Sequence

Table 11 shows the results of pull tests done on a sampling of cells made for delivery to JPL. Notice in all cases the pull test resulted in silicon being pulled when the contact separated. Performance of these cells appear satisfactory for a low cost solar cell approach, but full evaluation tests in actual panels will establish the process reliability.

Conclusion and Recommendations

A reliable copper contact system has been developed that will yield high quality low cost contacts to silicon solar cells. The final process plating sequence developed under this contract is a palladium - nickel - copper plating system. The system is described in general terms in Appendix I. Detailed process specifications for the final Pd-Ni-Cu system has been documented and sent to JPL under separate cover. Process specifications can be obtained from the LSA-PP & E area of JPL as part of their Technology Transfer Program. The costing of the process is determined by the SAMICS Format A's of Appendix (L). Further studies are required to establish the reliability of the

TABLE 10
SINTERING STUDY RESULTS*
PLATED Pd-Ni-Cu CONTACTS

TIME	TEST	TEMPERATURES		
		300°C	350°C	400°C
5 min.	Voc	0	+4mV	+2mV
	Isc	0	+.3ma	0
	CFF	0	+.01	+.02
15 min.	Voc	0	+3mv	-447mv
	Isc	+.2ma	+.5ma	-2.1ma
	CFF	-.01	-.01	-.40

*Table shows the average change of each group.

Groups consisted of three cell sets.

TABLE 11
PULL TESTS

CONTACT ADHESION

CONTACT TYPE	MODE	AREA	PULL STRENGTH	
			FRONT (grams)	BACK (grams)
Ti-Pd-Ag	EVAPORATED	.02cm ²	200 *	236 +
Pd-Ni-Cu Test 1 (1 cell)	PLATED	.02cm ²	200 *	200 *
Test 2 (1 cell)	PLATED	.02cm ²	300 +	300 *
Test 3 (1 cell)	PLATED	.02cm ²	Broke Wire	400 *

*PULLED SOME SILICON

+CELL BROKE

Cell Substrate: 7-14 ohm-cm P-type - Chemically Polished
Front - Al Alloyed Back

process in a production environment. It also may be possible for further cost reductions of the process by simplifications of the process, that is, a cheaper masking material, a one step adherent nickel plating, and a one step sintering process. Larger quantities of cells need to be analyzed and solar panels made and tested before the question of reliability can be determined.

REFERENCES

- 1) "Metallization of Large Silicon Wafers"
First Quarterly Report, JPL Contract No. 954689 (Motorola)
- 2) H.J. West, Prod. Fin., 26, 58 (April, 1962)
- 3) "Analysis of Copper Diffusion Through Different Metallic Barriers", Paper Study,
JPL Contract No. 955244 (Optical Coating Laboratory, Inc., ASEC)
- 4) "Effects of Impurities and Processing on Silicon Solar Cells". Tenth Quarterly
Report, JPL Contract No. #954331 (Westinghouse).

MILESTONE CHART

TASK	MONTH											
	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR		
COPPER PLATING SYSTEM												
A. Adhesion												
B. Contact Resistance												
C. Shadowing Effect												
D. Junction Shunting Effects												
PROCESS CONTROL												
A. Solution Control												
B. Effective Plating Rate												
C. Corrosion Resistance												
D. Solderability												
E. Mask Compatibility												
F. Simultaneous Deposition												
G. Scale-Up												
H. Preliminary Cost Estimate												
PLATING VARIABLES												
A. Different Solution Conditions												
B. Different Sensitizing Conditions												
C. Silicon Surface Preparation												
CONTACT BUILD-UP												
A. Reflow Soldering												
B. Electrolytic Plating												
HEAT TREATMENTS												
SAMPLE CELLS												
EVALUATION TESTS												
A. Plating Thickness, Rate												
B. Plating Coverage												
C. Grain Size												
D. Contact Resistance												
E. Plating Resistance												
F. Contact Adhesion												
G. Corrosion Resistance												
H. Solderability												

LEGEND: Scheduled: 
 Continuing: 
 Completed: 

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TASK	MONTH											
	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR		
<u>EVALUATION OF DIFFERENT NICKEL SOLUTIONS</u>												
<u>SAMICS COST ANALYSES</u>												
A. Process Sequence												
B. Process Steps												
C. Updated												
<u>LOW COST PLATING MASK</u>												
<u>HEAT TREATMENT STUDY</u>												
A. Plated Cells												
<u>CORROSION PROTECTION</u>												
<u>TECHNICAL REVIEWS</u>												
A. Program Review	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
B. Design Review	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
C. Project Integration		▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
D. Project Workshop			▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
<u>DOCUMENTATION</u>												
A. Program Plan		▲	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
B. Monthly Reports (Technical, Financial)			▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
C. Quarterly Technical report				▲	▲	▲	▲	▲	▲	▲	▲	▲
D. Draft Final Report					▲	▲	▲	▲	▲	▲	▲	▲
E. Final Report						▲	▲	▲	▲	▲	▲	▲

LEGEND:

Scheduled: 
 Continuing: 
 Completed: 

APPENDIX A

GOLD CYANIDE SOLUTION

200 ml Deionized Water

2 gm Gold Cyanide

10 ml 48% HF

Use at room temperature under a bright light for 2 minutes.

This solution was discussed on Page 11. Use was discontinued due to high cost.

APPENDIX B

COMMERCIAL PLATING SYSTEM

- A) Dynaplate Activator 120
- B) Dynaplate Conditioner 101
- C) Dynaplate 240 Electroless Copper

All solutions made by Thiokol/Dynachem Corporation.
Use at room temperature.

This bath is used in the final contact sequence, but only Bath C. The thin layer of copper generated from this bath, makes the electrolytic copper adhere better. See Process Specifications for Baseline Procedures, May 31, 1979, Contract No. 955244.

APPENDIX C

ELECTROLESS CHROMIUM BATHS

Bath A

Chromium Fluoride	15	gm/l
Chromium Chloride	1	gm/l
Sodium Citrate	7.5	gm/l
Sodium Hypophosphite	7.5	gm/l

The operating temperature was 85-95°C.

Bath B *

	<u>2x2 cm Cell</u>	<u>2 1/4" Cell</u>
Deionized Water	200 ml	1800 ml
Chromium Acetate	6 gm	42 gm
Nickel Acetate	.4 gm	28 gm
Sodium Citrate	8 gm	56 gm
Sodium Glycolate	8 gm	56 gm
Sodium Acetate	4 gm	28 gm
Sodium Hypophosphite	5 gm	35 gm

The operating temperature was 85-90°C.

*This bath formulation was selected for the final chromium plating sequence. See Process Specification Procedures for plating formulations and operating conditions, Contract No. 955244, dated May 31, 1979.

Formulations taken from "Electroless Plating Today" by Dr. Edward B. Saubestre.

APPENDIX D

ELECTROLYTIC COPPER SOLUTION

Deionized Water 1000 ml

H_2SO_4 30 ml

$CuSO_4$ 200 ml

Solution used at room temperature. Cells plate ~.3 microns per minute at 7 mA/cm².

This solution was used in final contact sequence. See Process Specifications for Baseline Procedures, May 31, 1979, Contract No. 955244.

APPENDIX E

MOTOROLA'S PLATING SOLUTIONSImmersion Palladium Bath*

	<u>2x2 cm Cell</u>	<u>2 1/4" Cell</u>	<u>3" Cell</u>
Deionized Water	300 ml	1800 ml	2400 ml
PdCL	.05 gm	.3 gm	.4 gm
HCL	1 ml	6 ml	8 ml
NH ₄ F	20 ml	120 ml	160 ml

Mixed in a sonic bath and used at room temperature in the dark.

Electroless Palladium Plating Bath⁺

Deionized Water	830 ml
HCL	4 ml
PdCL ₂	2 gm
NH ₄ CL	27 gm
NAH ₂ PO _d 2H ₂ O	6 gm
NH ₄ OH	160 ml

*Bath was used in final process. See Process Specification Procedures for plating formulations and operating conditions, Contract No. 955244, dated April 31, 1980.

⁺Bath only used for certain experiments. Palladium costs were too high.

APPENDIX F

CHROMIUM-COPPER PLATED CONTACT PROCEDURE

1. Standard 2x2 cm substrates or 2 1/4" cells.
2. Photoresist and etch.
3. Immersion palladium bath (Appendix E).
 - a) Five (5) seconds 6% HF.
 - b) Immersion palladium bath for 5 minutes in the dark.
 - c) Scrub cell with Q-tip, deionized water rinse.
 - d) Remove photoresist with acetone.
 - e) Heat treat 15 minutes at 400°C in N₂.
4. Electroless chromium bath (Appendix C).
 - a) Five (5) seconds 6% HF.
 - b) Deionized water rinse 5 seconds.
 - c) Immerse cells for 15 minutes, rinse deionized water.
 - d) Heat treat 15 minutes at 400°C in H₂.
5. Dip in 6% HF 5 seconds and then 5 seconds dip in deionized water.
6. Immerse in Dynachem electroless copper solution for 5 minutes at 35°C.
7. Plate in electrolytic copper solution for 20 minutes at (7 mA/cm²) for plating front and back simultaneously. Procedure plates 4-6 microns of dense copper.

For more detailed procedure see Process Specification Procedures, Contract No. 955244, dated May 31, 1979.

APPENDIX G

PLATED PALLADIUM-PLATED COPPER PROCEDURES

1. Standard 2x2 cm substrates.
2. Photoresist and etch.
3. Immersion palladium bath (Appendix E).
 - a) Five (5) seconds 6% HF.
 - b) Immersion palladium bath for 5 minutes.
 - c) Scrub with Q-tip, deionized water rinse.
4. Electroless palladium bath (Appendix E)
 - a) Five (5) seconds in 6% HF.
 - b) Immerse in bath for 2 minutes at 40°C.
 - c) Heat treat 400°C in N₂ for 15 minutes.
5. Dip in 6% HF for 5 seconds and rinse in deionized water for 5 seconds.
6. Electroless copper bath (Appendix B) for 2 minutes.
7. Electrolytic copper bath (Appendix D)
 - a) Twenty (20) minutes at 7 mA/cm² for 4-6 microns layer.

Process abandoned in favor of Pd-Cr-Cu of Appendix F largely because Pd-Cr-Cu is a more cost effective plating sequence.

APPENDIX H

ELECTROLESS NICKEL SOLUTION

**Solution #139-500011-71 Electroless Nickel Solution obtained from
J.E. Halma Company Inc., 91 Dell Glen Avenue, Lodi, N.J., 07644**

Solution is poured full strength into a heated glass vessel the appropriate size. Ammonium hydroxide is added until the ph is ~8.2. The solution is maintained at 90°C and kept covered to avoid excessive evaporation.

APPENDIX I

PROCESSES AND PROCEDURES FOR CONTACTING SILICON
SOLAR CELLS WITH A PALLADIUM-NICKEL-COPPER PLATING SYSTEM

PROCESS SPECIFICATIONS

APRIL 31, 1980

JPL CONTRACT NO. 955244

PREFARED BY D.P. TANNER

OPTICAL COATING LABORATORY, INC.
PHOTOELECTRONICS DIVISION
15251 EAST DON JULIAN ROAD
CITY OF INDUSTRY, CA. 91746

INTRODUCTION

A final copper-based contact system has been developed of which this document will detail the process. The system does simultaneous deposition of base metals on the front and back of the cells. First an immersion palladium bath (1) is used, which deposits ~40 angstroms of palladium on the desired areas of the cell. This layer is sintered and the top nonadherent surface material is removed chemically. Next an electroless nickel bath is used which deposits ~2000 angstroms of nickel. Nickel has been shown to be a good conductor and excellent barrier to copper diffusion. The last layer is an electrolytic copper layer plated to a thickness of 4 to 6 microns. Then the nickel and copper layer is sintered for good adhesion and to establish the reliability of the copper barrier.

The process (chemical baths and fixturing) is now set-up for 3" diameter cells. This report will sequence the process, list the chemicals used, the mixing procedures, and relate the timing of each step.

The plating cell material used was 7-14 ohm-cm, p-type silicon approximately 12 mils thick. Cells had a 25 ohm/square phosphorus diffusion on the chemically polished front and a printed aluminum paste alloy on the back, giving the backs a rough surface as well as a back surface field.

The plating system has been developed on a laboratory scale process. Problems involved in scaling up to a production level have not been investigated.

(1) Base immersion palladium bath was developed at Motorola, JPL
Contract No. 954689.

CHEMICALS

o WET

Acetone, Electronic Grade

Ammonium Fluoride 40% NH_4F , Electronic Grade

Ammonium Hydroxide, NH_3OH , Electronic Grade

Deionized Water

Electroless Ni Solution #139-500011-71*

Hydrochloric Acid, 37% HCl, Electronic Grade

Hydrofluoric Acid, 48% HF, Electronic Grade

Nitric Acid, HNO_3 , Electronic Grade

Plating Resist, ER-6055**

Plating Resist Reducer, ER-48073

Sulfuric Acid, H_2SO_4 , Electronic Grade

Trichlorethylene, Electronic Grade

o DRY

Copper Sulfate, Reagent Grade

Palladium Chloride, 99.9% Anhydrous

*Obtained from J.E. Halma Company, Inc., 91 Dell Glen Ave., Lodi, NJ 07644.

**Obtained from Colonial Printing Ink Company, 180 E. Union Ave., E. Rutherford, NJ 07073

EQUIPMENT LIST

- Plastic or Pyrex Trays
- Plastic Cassette Wafer Holders
- Thermometers
- Timers
- Hot Plates (with temperature controls)
- Plastic Tweezers
- Exhaust Hoods
- Protective Clothing
- Plastic Graduated Cylinders
- Sintering Furnace (Lindberg Model 55773)
- Quartz Boats
- Power Supply (0-20 volts, 0-10 amps)
- Heat Lamp
- Ph Meter
- Screen Printer (Forslund Model 35-00)

EQUIPMENT AND FACILITIES

A laboratory size screen printer (8"x 12" screen) was used to print on the plating resist. This machine required manual operation, but the process proved to be relatively simple, enabling us to print several cells per minute.

The plating experiments were done in exhaust hoods, even though only one of the solutions (Ni bath) seemed to give off fumes. Certainly, a production scale plating set-up, should be in a well vented area.

All plating baths containing hydrofluoric acid should be in plastic containers, for which we used polyethylene trays. The nickel bath was in pyrex tray which could be heated. Rinse water was continuously flowing in plastic trays.

The cells were held in plastic cassette wafer carriers during the actual plating steps. For the heat treatments, cells were manually loaded onto quartz boats, a procedure that can be modified in the future to a direct dump transfer process when large furnace tubes are used.

Heat treatments were done in resistively heated quartz tubes in a nitrogen only atmosphere.

Finally, the electrolytic bath used a power supply (20 volts, 0-10 amps) to plate-up the copper layer.

SOLUTION PREPARATION

- Dilute Hydrofluoric (6% Solution)

Mix 2400 ml of deionized (DI) water with 336 ml of 48% electronic grade hydrofluoric acid. A covered plastic tray is used in the sequence.

- Immersion Palladium

DI water (2400 ml) is mixed with .64 gm of palladium chloride in a plastic tray which is then placed in a sonic bath. Eight (8) ml of hydrochloric acid is then added, followed by 120 ml of ammonium fluoroide. The solution is mixed in the sonic bath for 30 minutes. The solution should be allowed to stand for several hours before use, and is kept covered when not in use.

- Aqua Regia

This solution is mixed in a ratio of HNO_3 to HCL of 1:1. This solution should be mixed one hour before use.

- Electroless Nickel Solution

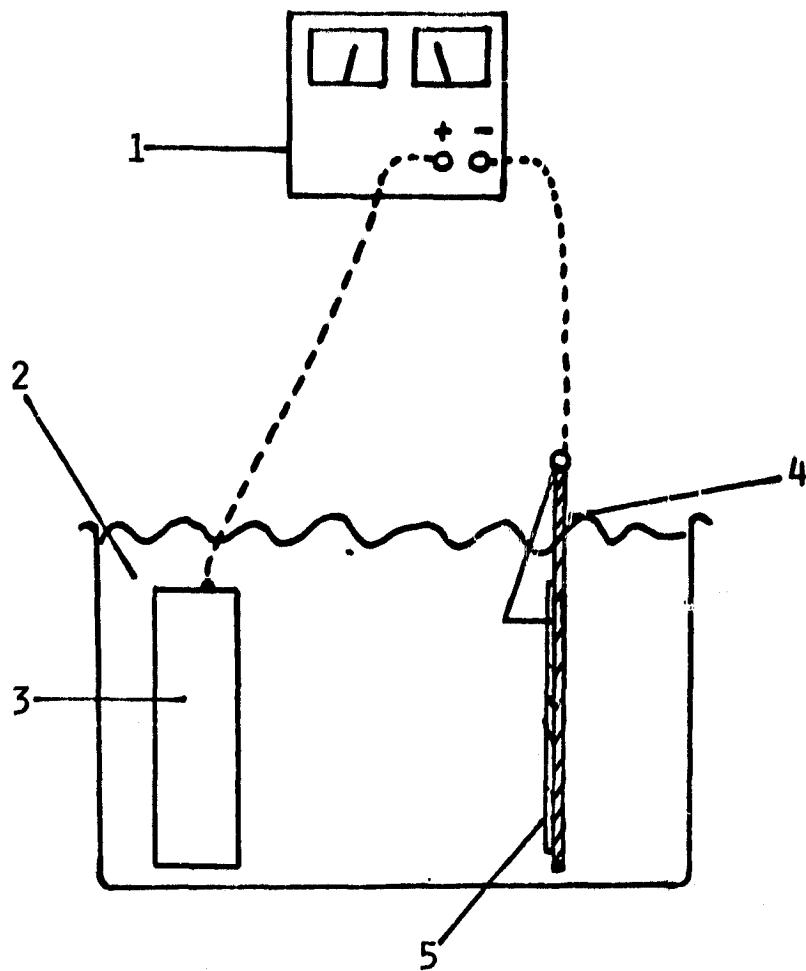
This solution is mixed in a pyrex tray to allow heating to its operating temperature of 90°C . Four thousand (4,000) ml of the premixed electroless nickel solution is mixed with a small amount of ammonium hydroxide until the ph is 8.2 (monitored by a ph meter). Over 50 3" diameter cells have been plated from one solution.

- Electrolytic Copper

The electrolytic copper solution consists of 6000 ml of DI water, 60 ml of sulfuric acid, and 1200 gms of copper sulfate. The anode (+) is a massive

copper block in which the cells are the cathodes (-) (see Figure 1). Power supply requirements are adjusted to accommodate plating of the desired number of cells.

FIGURE 1



ELECTROLYTIC COPPER BATH

1. Power Supply
2. Copper Solution
3. Copper Block
4. Cell Holder With Clip
5. Cell

PRINT-ON PLATING MASK PROCEDURES

1. Add 5% by volume of the reducer ER-48073 to the ER-6055 plating resist and mix.
2. Silk Screen the resist on the top surface of the cells using a 1/8" distance between the screen and the cells.
3. Dry cells under heat lamp (G.E. Infrared Heat Reflector Lamp, 250W) at a 2 ft. distance for 5 minutes.
4. The cells are ready for plating.

Mask Material: ER-6055 Blue H.B. Fine Line Plating Resist

Reducer: ER-48073

Company: Colonial Printing Ink Company
180 E. Union Avenue
E. Rutherford, N.J. 07073

PRE-BATH PREPARATION

The cells before plating are prepared so the plating will form proper contacts.

The basic process sequence is as follows:

- (A) Cells are diffused and have aluminum alloy BSF.
- (B) The fronts are then coated with 5000 angstroms of CVD SiO₂ for a plating mask.
- (C) The fronts are printed with the plating resist and a metallization pattern is etched into the CVD SiO₂.
- (D) The plating resist is left on, to mask the cell from the immersion palladium bath. The SiO₂ is the mask for the nickel and copper baths.

PROCESS SEQUENCE

NOTE: All baths, rinses, and sintering times are not critical. They may be varied $\pm 5\%$ with no effect to the plating process. Unless otherwise specified, solutions, mixtures, rinses, are at ambient temperatures.

1.0 IMMERSION PALLADIUM

- 1.1 Load cells (which have been printed with plating resist) into cassette holder (25 cells per cassette).
- 1.2 Etch CVD through pattern defined by plating mask. Place in 6% HF solution for 5 minutes.
- 1.3 Directly place the cassette into the immersion palladium solution for 5 minutes. This plating is done in the dark while continuously agitating the solution.
- 1.4 Rinse for 2 minutes in DI water.
- 1.5 Remove plating mask in trichlorethylene for 2 minutes in a sonic bath.
- 1.6 Rinse cassette in acetone for 30 seconds.
- 1.7 Dry under heat lamp (1 minute).

2.0 SINTERING

- 2.1 Load quartz boat.
- 2.2 Heat treat at $400 \pm 1^\circ\text{C}$ for 10 minutes in a nitrogen atmosphere.
- 2.3 Remove boat from hot zone of furnace and allow to cool with nitrogen gas flow for 3 minutes in the cold zone of the furnace.
- 2.4 Transfer cells back to cassette holder.

3.0 AQUA REGIA

- 3.1** Quickly dip the cassette in this solution for 2 seconds to remove non-adherent palladium material.
- 3.2** Immediately rinse with DI water for 5 minutes to remove all traces of the surface etch.

4.0 ELECTROLESS NICKEL BATH

- 4.1** Place the cassette of cells in the 6% HF solution for 5 seconds, then 5 seconds in the DI water rinse.
- 4.2** Place the cells immediately in the nickel bath for 6 minutes. The bath temperature is maintained at $90^{\circ}\text{C} \pm 2$. Agitate the cassette every minute to remove bubbles formed from the plating, nitrogen bubbling is recommended for bath agitation.
- 4.3** Rinse in DI water 2 minutes.

5.0 ELECTROLYTIC COPPER

- 5.1** Place cells in plating fixture.
- 5.2** Dip fixture in the 6% HF solution 5 seconds.
- 5.3** Rinse in DI water 5 seconds.
- 5.4** Place cells in copper bath and attach + to block, - to cell holder as in sketch of Figure (1).
- 5.5** Plate all fronts at 300 mA cell for 10 minutes.
- 5.6** Plate cell backs at 900 mA per cell for 10 minutes.
- 5.7** Rinse in DI water for 3 minutes and blow dry.

6.0 SINTERING

- 6.1 Load quartz boat.
- 6.2 Sinter at $300^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 5 minutes in a nitrogen atmosphere.

NOTE: The sintering step improves adhesion and in addition kills cells which have a potential for copper diffusion through pin-hole leaks in the nickel barrier.

- 6.3 Remove boat from hot zone of furnace and allow to cool with nitrogen gas flow for 3 minutes in the cold zone of the furnace.
- 6.4 Transfer cells back to holder.

7.0 EDGE GRIND (OPTIONAL)

- 7.1 Grind edges of cell while spinning by holding an abrasive material to the edge.
- 7.2 Test cells.

APPENDIX J

PRINT-ON PLATING MASK PROCEDURES

1. Add 5% by volume of the reducer ER-48073 to the ER-6055 plating resist and mix.
2. Silk screen the resist on the top surface of the cells using a 1/8" distance between the screen and the cells.
3. Dry cells under heat lamps at a 2 ft. distance for 5 minutes.
4. The cells are ready for plating.

Mast Material: ER-6055 Blue H.B. Fine Line Plating Mask

Reducer: ER-48073

Company: Colonial Printing Ink Company
180 E. Union Avenue
E. Rutherford, N.J. 07073

APPENDIX K

DEVELOPMENT OF LOW COST CONTACTS TO SILICON SOLAR CELLS

SAMICS REPORT NO. 2

FOR PERIOD COVERING
15 OCTOBER 1978 TO APRIL 1980

By

D.P. TANNER AND P.A. ILES

JPL CONTRACT NO. 955244

OPTICAL COATING LABORATORY, INC.
PHOTOELECTRONICS DIVISION
15251 EAST DON JULIAN ROAD
CITY OF INDUSTRY, CA. 91746

"The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effect toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

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A. INTRODUCTION

This is the second (and final) Solar Arrays Manufacturing Industry Costing Standard (SAMICS) report on the plating system developed for JPL contract No. 955244. The process electrolessly plates a thin palladium layer ($\sim 50\text{\AA}$), and a nickel layer ($\sim 2000\text{\AA}$). Then a electrolytically deposited copper layer (~ 5 microns) is plated for the main current collection of the cell.

The process sequence is defined on Table 1 and was used to generate the data on the format A's of the SAMICS study. This process has been shown to work on a laboratory scale, but certain assumptions must be made for the production scale for the proper costing to be made. These assumptions are detailed in the next section.

B. ASSUMPTIONS

The process is detailed on page 84. Several changes have been made to cost the process as a production process and not a laboratory scale one.

- a) A high throughput screen printing machine was assumed (taken from JPL Document #1012-78/17) instead of the slow manual printer we used in the laboratory.
- b) All sinterings were done in a standard tube furnace, but a high throughput belt type furnace will be assumed for the proper costing.
- c) The laboratory process used a solvent (trichlorethylene) removable plating mask material whereas in the production costing, a caustic removable plating mask will be assumed.
- d) The nickel bath used was purchased from J.E. Halma Co., which was bought only in small quantities. The nickel bath formulation in Motorola

Report #234412 closely matches the one used so these "chemical only" costs were assumed.

- e) On the laboratory scale the cells were electrolytically plated in two steps, first the front, then the back. It was assumed with the proper fixturing this could be done in one step (front and back simultaneously).
- f) The contact process was costed using 110% cell contact coverage (10% on the front and 100% on the back). A total of only 30% is required for good solar cell performance (10% on the front and 20% on the back), but this process requires 2 masking steps which proved to be more expensive than the extra metal used.
- g) Only three (3) inch diameter cells (7.6 cm) will be costed since this was the cell size used in the laboratory study.
- h) Many other assumptions were taken from the Motorola report #234412 as well as dollar values for equipment costs and replacement time for chemicals.

Each format A will include the basic assumptions for each particular step and as an example process Pd-plate will show the calculation of all values.

PALLADIUM - NICKEL - COPPER CONTACT SYSTEM

SAMICS Format A Process Summary

INPUT Product: Wafers

OUTPUT Product: Cell

<u>STEP</u>	<u>FORMAT A PROCESS</u>	<u>INPUT PRODUCT</u>	<u>OUTPUT PRODUCT</u>
1	MASKFT	WAFERS	WAFERA
2	PdPLATE	WAFERA	WAFERB
3	SINTERA	WAFERB	WAFERC
4	NIPLATE	WAFERC	WAFERD
5	CuPLATE	WAFERD	WAFERE
6	SINTERB	WAFERE	CELL

COST ACCOUNT CATALOG

<u>CATALOG NUMBER</u>	<u>ITEM DESCRIPTION</u>	<u>UNITS</u>	<u>PRICE/Q</u>	<u>YEAR</u>
EZ0100D	PLATING RESIST	GALLONS	\$20.00/gal.	1980
EZ0101D	SCREEN WASH	GALLONS	\$ 8.00/gal.	1980
EZ0102D	NITROGEN GAS (Evap. from Liquid)	Cu.Ft.	\$.00934/cu.ft.	1977
EZ0103D	NICKEL BATH	LITER	\$.37723*	1975
EZ0104D	COPPER BATH MAKE-UP	GALLON	\$3.96	1980
EZ0105D	COPPER BATH ADDITIVE	GALLON	\$18.75	1980

*TAKEN FROM MOTOROLA REPORT DOE/JPL #954689 - 78/2

PROCESS

Palladium-Nickel-Copper Plated Contacts

IPEG Analysis Baseline Process

1.
 - a) Screen print plating mask (front only).
 - b) Bake under heat lamp 3 minutes.
2.
 - a) Immerse in 6% hydrofluoric acid - 2 minutes.
 - b) Place in immersion palladium bath - 5 minutes.
 - c) DI H₂O rinse - 2 minutes.
3.
 - a) Remove plating mask - 2% NaOH solution - 30 seconds.
 - b) DI H₂O rinse - 2 minutes.
 - c) Isopropyl alcohol dry 40°C - 15 seconds.
4. Sinter at 400°C - 15 seconds.
5.
 - a) Aqua Regia dip - 2 seconds.
 - b) DI H₂O Rinse - 5 minutes.
 - c) Immerse in 6% hydrofluoric acid - 2 seconds.
 - d) DI H₂O rinse - 10 seconds.
 - e) Electroless nickel bath 90°C - 6 minutes.
 - f) DI H₂O rinse - 2 minutes.
6.
 - a) Electrolytic Copper Bath - 10 minutes.
 - b) DI Rinse - 2 minutes.

c) Isopropyl alcohol dry. 40°C - 15 seconds.

7. Sinter 300°C in N_2 for 5 minutes.

C. STANDARD SAMICS FORMATS

Format A

SOLAR ARRAY MANUFACTURING INDUSTRY COSTING STANDARDS

Page 1 of 6



FORMAT A — PROCESS DESCRIPTION

A-1 Process [Referent]

MASKFT

Note: Names given in brackets [] are the names of process attributes requested by the SAMIS computer program.

A 2 [Descriptive Name] of Process Screen Print Plating Resist on Front of cell, (90% coverage)

PART 1 — PRODUCT DESCRIPTION

A 3 [Product, Referent] WAFERA

A 4 Descriptive Name [Product, Name] Solar cell printed with mask material

A 5 Unit Of Measure [Product, Units] Wafers

PART 2 — PROCESS CHARACTERISTICS

A 6 [Output, Rate] (Not Throuput) 25 Units (given on line A-5) Per Operating Minute

A 7 [Inprocess, Inventory, Time] 20 Calendar Minutes (Used only to compute in-process inventory)

A 8 [Duty, Cycle] .976 Operating Minutes Per Minute

A 8a [Number, Of, Shifts, Per, Day] 1 Shifts

A 8b [Personnel, Integerization, Override, Switch] Off (Off or On)

PART 3 — EQUIPMENT COST FACTORS (Machine Description)

A 9 Component [Referent]	<u>SPSYSF*</u>
A 9a Component [Descriptive Name]	<u>Printer</u>
A 10 Base Year For Equipment Prices [Price, Year]	<u>1977</u>
A 11 [Purchase, Cost, Vs, Quantity, Bought, Table] (Number Of and \$ Per Component)	<u>\$ 50k</u>
A 12 Anticipated [Useful, Life] (Years)	<u>7</u>
A 13 [Salvage, Value] (\$ Per Component)	<u>\$ 20k</u>
A 14 [Removal, And, Installation, Cost] (\$/Component)	<u>\$ 1k</u>

Note: The SAMIS computer program also prompts for the [Payment, Float, Interval], the [Inflation, Rate, Table], the [Equipment, Tax, Depreciation, Method], and the [Equipment, Book, Depreciation, Method]. In the LSA SAMICS context, use 0.0, (1975 6.0 *), DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

*Taken from JPL Document #1012-78/17

A-15 Process Referent (From Front Side Line A-1) MASKED**PART 4 - DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)**

[Facility Or Personnel Requirement]

A-16

A-18

A-19

A-17

Catalog Number
(Expense Item
Referent)Amount Required
Per Machine (Per Shift)
[Amount. Per. Machine]

Units

Requirement Description or Name

A2080D

275

Sq. Ft.

Floor Space Type B

B3096D

0.25

Persons/Shift

Semiconductor Assembler

B3688D

.05

Persons/Shift

Electronics Maintenance

PART 5 - DIRECT REQUIREMENTS PER MACHINE PER MINUTE (SAMIS will ask first for Byproducts)

[Byproduct] and [Utility Or Commodity Requirement]

A-20

A-22

A-23

A-21

Catalog Number
(Expense Item
Referent)Amount Required
Per Machine Per Minute
[Amount. Per. Cycle]

Units

Requirement Description or Name

C1032B

0.4202

Kw. Hr/Min.

Electricity

E1576D

0.00688

Screens/Min.

Screens

E1624D

0.0583

Squeegee/Min.

Squegees

EZ0100D

.0015

Gal/Min.

Plating Resist

EZ0101D

.00022

Gal/Min.

Screen Wash.

D1176D

-.5

Cells/Min.

Rejected Cells

PART 6 - INTRA-INDUSTRY PRODUCT(S) REQUIRED

A-24

A-28

A-26

A-27

A-25

[Required Product]
(Reference)[Yield] *
(%)[Ideal, Ratio] ** Of
Units Out/Units In

Units Of A-26***

Product Name

WAFERS

.98

1/1

WAFERS/WAFERS

MASKED WAFER

PREPARED BY

DAVID P. TANNER

DATE

9/16/80

* 100% minus percentage of required product lost in this process.

** Assume 100% yield here.

*** Examples: Modules/Cell or Cells/Wafer.

MANUFACTURED
BY MASKED WAFER CO.
FOR HIGH RELIABILITY



FORMAT A — PROCESS DESCRIPTION

JPL PROPULSION LABORATORY
California Institute of Technology
4800 Oak Grove Drive, Pasadena, Calif. 91109

A-1 Process (Referent)

PDPLATE

Note: Names given in brackets [] are the names of process attribute requested by the SAMIS computer program.

A 2 [Descriptive Name] of Process Plate Pd metal on front and back of the cells

PART 1 — PRODUCT DESCRIPTION

A-3 [Product, Referent] WAFERB

A-4 Descriptive Name [Product, Name] Wafers plated with palladium metal

A-5 Unit Of Measure [Product, Units] Wafers

PART 2 — PROCESS CHARACTERISTICS

A-6 [Output, Rate] (Not Thruput) 33.33 Units (given on line A-5) Per Operating Minute

A-7 [Inprocess, Inventory, Time] 12 Calendar Minutes (Used only to compute in-process inventory)

A-8 [Duty, Cycle] .99 Operating Minutes Per Minute

A-8a [Number, Of, Shifts, Per, Day] Shifts

A-8b [Personnel, Integerization, Override, Switch] (Off or On)

PART 3 — EQUIPMENT COST FACTORS (Machine Description)

A-9 Component [Referent]	Chemhood	Solvhood
A-9a Component [Descriptive, Name]	<u>Chemical hood with replenish system</u>	<u>Solvent hood</u>
A-10 Base Year For Equipment Prices [Price, Year]	<u>1977</u>	<u>1977</u>
A-11 [Purchase, Cost, Vs, Quantity, Bought, Table] (Number Of and \$ Per Component)	<u>\$12k</u>	<u>\$4.5K</u>
A-12 Anticipated [Useful, Life] (Years)	<u>7</u>	<u>7</u>
A-13 [Salvage, Value] (\$ Per Component)	<u>\$1.2k</u>	<u>\$450</u>
A-14 [Removal, And, Installation, Cost] (\$/Component)	<u>\$200</u>	<u>\$200</u>

Note: The SAMIS computer program also prompts for the [Payment, Float, Interval], the [Inflation, Rate, Table], the [Equipment, Tax, Depreciation, Method], and the [Equipment, Book, Depreciation, Method]. In the LSA SAMICS context, use 0.0, (1975 6.0 *), DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

A-15 Process Referent (From Front Side Line A-1) PdPLATE**PART 4 - DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)**

[Facility Or Personnel Requirement]

A-16

A-18

A-19

A-17

Catalog Number
(Expense Item
Referent)Amount Required
Per Machine (Per Shift)
(Amount. Per. Machine)

Units

Requirement Description or Name

A2080D
B3672D90
1Sq. Ft.
Person/ShiftMfg. Space (Type B)
Chemical Operator II 55885**PART 5 - DIRECT REQUIREMENTS PER MACHINE PER MINUTE (SAMIS will ask first for Byproducts)**

[Byproduct] and [Utility Or Commodity Requirement]

A-20

A-22

A-23

A-21

Catalog Number
(Expense Item
Referent)Amount Required
Per Machine Per Minute
(Amount. Per. Cycle)

Units

Requirement Description or Name

G1052D
E1320D
G1054D.0168
.00023
.004601Gms/Min.
Lbs/Min.
Lbs/Min.PdCL+
HCL
NH₄FE1352D
E1328D
C1144D.0176
.00513
.81339Gals/Min.
Lbs/Min.
Cu. Ft.IPA
HF
DI H₂OC10322B
D1176D.0444
.0667Kwh/Min.
Cells/Min.Electricity
Rejected Cells

E1600D

.000012

Lbs/Min.

NaOH

PART 6 - INTRA-INDUSTRY PRODUCT(S) REQUIRED

A-24 (Required Product) (Reference)	A-28 (Yield) * (%)	A-26 (Ideal. Ratio) ** Of Units Out/Units In	A-27 Units Of A-26***	A-25 Product Name
WAFERA	99.8	1.0	WAFERS/WAFERS	PdPLATED WAFER

PREPARED BY

DAVID P. TANNER

DATE

9/16/80

*100% minus percentage of required product lost in this process.

**Assume 100% yield here.

***Examples: Modules/Cell or Cells/Wafer.

†Calculated from Motorola Report No. 234412
See Appendix For Calculations



SOLAR ARRAY MANUFACTURING INDUSTRY COSTING STANDARDS

Page 3 of 6

FORMAT A — PROCESS DESCRIPTION

JPL PROPULSION LABORATORY
Chemical and Technical
Data and Cost Data / Products Data System

A-1 Process (Referent)

SINTERA

Note: Names given in brackets [] are the names of process attributes requested by the SAMIS computer program.

A-2 [Descriptive Name] of Process Sinter the plated palladium layer.

PART 1 — PRODUCT DESCRIPTION

A-3 [Product, Referent] WAFERC

A-4 Descriptive Name [Product, Name] Sintering of palladium layer

A-5 Unit Of Measure [Product, Units] Cells

PART 2 — PROCESS CHARACTERISTICS

A-6 [Output, Rate] (Not Thruput) 200 Units (given on line A-5) Per Operating Minute

A-7 [Inprocess, Inventory, Time] 10 Calendar Minutes (Used only to compute in-process inventory)

A-8 [Duty, Cycle] .99 Operating Minutes Per Minute

A-8a [Number, Of, Shifts, Per, Day] Shifts

A-8b [Personnel, Integerization, Override, Switch] (Off or On)

PART 3 — EQUIPMENT COST FACTORS (Machine Description)

A-9 Component (Referent) Furnace

A-9a Component [Descriptive, Name]

A-10 Base Year For Equipment Prices [Price, Year] 1977

A-11 [Purchase, Cost, Vs, Quantity, Bought, Table] (Number Of and \$ Per Component) \$35K

A-12 Anticipated [Useful, Life] (Years) 7

A-13 [Salvage, Value] (\$ Per Component) \$3.5K

A-14 [Removal, And, Installation, Cost] (\$/Component) \$1K

Note: The SAMIS computer program also prompts for the [Payment, Float, Interval], the [Inflation, Rate, Table], the [Equipment, Tax, Depreciation, Method], and the [Equipment, Book, Depreciation, Method]. In the LSA SAMICS context, use 0.0, (1975 6.0 *), DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

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SOLAR ARRAY MANUFACTURING INDUSTRY COSTING STANDARDS

Page .. 4 of ..

FORMAT A -- PROCESS DESCRIPTION

JPL PROPULSION LABORATORY
1450 One NASA Drive, MS 200-100
JPL, Pasadena, California 91109

A-1 Process (Referent)

NIPLATE

Note. Names given in brackets [] are the names of process attribute requested by the SAMIS computer program.

A 2 [Descriptive Name] of Process Plate nickel on front and back of the cells.

PART 1 - PRODUCT DESCRIPTION

A 3 [Product, Referent] WAFERD

A 4 Descriptive Name [Product Name] Wafers with plated nickel layer.

A 5 Unit Of Measure [Product, Units] Cells

PART 2 - PROCESS CHARACTERISTICS

A 6 [Output, Rate] (Not Thruput) 22.68 Units (given on line A-5) Per Operating Minute

A 7 [Inprocess, Inventory, Time] 13 Calendar Minutes (Used only to compute in-process inventory)

A 8 [Duty, Cycle] .99 Operating Minutes Per Minute

A-8a [Number, Of, Shifts, Per, Day] Shifts

A-8b [Personnel, Integerization, Override, Switch] (Off or On)

PART 3 - EQUIPMENT COST FACTORS (Machine Description)

A-9 Component [Referent]	<u>CHEMHOOD</u>	<u>CHEMFELW</u>	
A-9a Component [Descriptive, Name]	<u>Chemical Hood</u>	<u>Hood with replenish system</u>	
A 10 Base Year For Equipment Prices [Price, Year]	<u>1977</u>	<u>1977</u>	
A-11 [Purchase, Cost, Vs, Quantity, Bought, Table] (Number Of and \$ Per Component)	<u>\$4.5K</u>	<u>\$12K</u>	
A-12 Anticipated [Useful, Life] (Years)	<u>7</u>	<u>7</u>	
A-13 [Salvage, Value] (\$ Per Component)	<u>\$450</u>	<u>\$1.2K</u>	
A-14 [Removal, And, Installation, Cost] (\$/Component)	<u>\$200</u>	<u>\$200</u>	

Note: The SAMIS computer program also prompts for the [Payment, Float, Interval], the [Inflation, Rate, Table], the [Equipment, Tax, Depreciation, Method], and the [Equipment, Book, Depreciation, Method]. In the LSA SAMICS context, use 0.0, (1975 6.0 *), DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

A 15 Process Referent (From Front Side Line A-1) NiPLATE

PART 4 - DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)

[Facility Or. Personnel Requirement]

A 16

A-18

A-19

A-17

Catalog Number
(Expense Item
Referent)Amount Required
Per Machine (Per Shift)
(Amount. Per. Machine)

Units

Requirement Description or Name

A2080D
B3672D90
1Sq. Ft.
Person/Shift

Mfg. Space (Type B)

Chemical Operator II 55885

PART 5 - DIRECT REQUIREMENTS PER MACHINE PER MINUTE (SAMIS will ask first for Byproducts)

[Byproduct] and [Utility, Or. Commodity Requirement]

A 20

A-22

A-23

A-21

Catalog Number
(Expense Item
Referent)Amount Required
Per Machine Per Minute
(Amount. Per. Cycle)

Units

Requirement Description or Name

E1320D
E1400D.01317
.01317Gal/Min.
Gal/Min.HCL
HNOE1328D
EZ0103D
CT144D.00513
.0906
.802Lbs/Min.
Liter/Min.
CU. Ft./Min.HF³
NI Bath⁺
DI H₂OC1032B
D1176D.03432
.2268KwH/Min.
Cells/Min.Electricity
Rejected Cells

PART 6 - INTRA-INDUSTRY PRODUCT(S) REQUIRED

A 24

[Required. Product
(Reference)]

A 28

[Yield] *
(%)

A-26

[Ideal. Ratio] ** Of
Units Out/Units In

A-27

Units Of A-26***

A-25

Product Name

WAFER

99.0

1.0

WAFERS/WAFERS

NiPlated Wafers

PREPARED BY

DAVID P. TANNER

DATE

9/16/80

*100% minus percentage of required product lost in this process.

**Assume 100% yield here.

***Examples: Modules/Cell or Cells/Wafer.

+Taken from Motorola Report #954689



SOLAR ARRAY MANUFACTURING INDUSTRY COSTING STANDARDS

Page 5 of

FORMAT A — PROCESS DESCRIPTION

JPL PROPULSION LABORATORY
Code 500, Building 200, Room 200
4800 Oak Grove Dr., Pasadena, Calif. 91109

A-1 Process (Referent)

CuPLATE

Note: Names given in brackets [] are the names of process attributes requested by the SAMIS computer program.

A-2 [Descriptive Name] of Process Plate electrolytic copper on the deposited nickel

PART 1 — PRODUCT DESCRIPTION

A-3 [Product, Referent] WAFERE

A-4 Descriptive Name [Product, Name] Wafers with plated copper layer

A-5 Unit Of Measure [Product, Units] Cells

PART 2 — PROCESS CHARACTERISTICS

A-6 [Output, Rate] (Not Thruput) 6.66 Units (given on line A-5) Per Operating Minute

A-7 [Inprocess, Inventory, Time] 10 Calendar Minutes (Used only to compute in-process inventory)

A-8 [Duty, Cycle] .99 Operating Minutes Per Minute

A-8a [Number, Of Shifts, Per, Day] Shifts

A-8b [Personnel, Integerization, Override, Switch] (Off or On)

PART 3 -- EQUIPMENT COST FACTORS (Machine Description)

A-9 Component [Referent]	Plater	RINSETK
A-9a Component [Descriptive, Name]	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
<u> </u>	<u> </u>	<u> </u>
A-10 Base Year For Equipment Prices [Price, Year]	<u>1978</u>	<u>1977</u>
A-11 [Purchase, Cost, Vs, Quantity, Bought, Table] (Number Of and \$ Per Component)	<u>\$5100</u>	<u>\$4.5K</u>
A-12 Anticipated [Useful, Life] (Years)	<u>7</u>	<u>7</u>
A-13 [Salvage, Value] (\$ Per Component)	<u>\$510</u>	<u>\$450</u>
A-14 [Removal, And, Installation, Cost] (\$/Component)	<u>\$200</u>	<u>\$200</u>

Note: The SAMIS computer program also prompts for the [Payment, Float, Interval], the [Inflation, Rate, Table], the [Equipment, Tax, Depreciation, Method], and the [Equipment, Book, Depreciation, Method]. In the LSA SAMICS context, use 0.0, (1975 6.0 *), DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

A-15 Process Referent (From Front Side Line A-1) CUPLADE

PART 4 – DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)

(Facility, Or, Personnel Requirement)

A-16 Catalog Number (Expense Item Referent)	A-18 Amount Required Per Machine (Per Shift) (Amount, Per. Machine)	A-19 Units	A-17 Requirement Description or Name
A2064D	.75	Sq. Ft.	Mfg. Space (Type A)
B3672D	.25	Person/Shift	Chemical Operator II 55885
B3688D	.05	Persons/Shift	Electronics Maintenance

PART 5 – DIRECT REQUIREMENTS PER MACHINE PER MINUTE (SAMIS will ask first for Byproducts)

[Byproduct] and [Utility, Or, Commodity Requirement])

A-20 Catalog Number (Expense Item Referent)	A-22 Amount Required Per Machine Per Minute (Amount, Per. Cycle)	A-23 Units	A-21 Requirement Description or Name
EZ104D	.00421	Gal/Min.	Cu Bath Make-Up
EZ105D	.00104	Gal/Min.	Cu Bath Additive
C1032D	.2	kwh/Min.	Electricity
D1176D	-.0666	Cells/Min.	Rejected Cells
D1032D	-.01041	Gal/Min.	Wasted Acid
C1144D	.0802	Cu. ft./Min.	DI H ₂ O
E1352D	.0035	Gal/Min.	IPA

PART 6 – INTRA-INDUSTRY PRODUCT(S) REQUIRED

A-24 [Required Product (Reference)]	A-28 [Yield] * (%)	A-26 [Ideal. Ratio] ** Of Units Out/Units In	A-27 Units Of A-26***	A-25 Product Name
WAFERD	99.0	1.0	WAFERS/WAFERS	CuPlated Wafers

PREPARED BY

DAVID P. TANNER

DATE

9/16/80

* 100% minus percentage of required product lost in this process.

** Assume 100% yield here.

***Examples: Modules/Cell or Cells/Wafer.

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FORMAT A — PROCESS DESCRIPTION

A-1 Process (Referent)
SINTERB

Note: Names given in brackets [] are the names of process attributes requested by the SAMIS computer program.

A-2 [Descriptive. Name] of Process Final sintering step for plated copper contacts.

PART 1 — PRODUCT DESCRIPTION

A-3 [Product. Referent] Cells

A-4 Descriptive Name [Product. Name] Solar Cells utilizing copper plated contacts.

A-5 Unit Of Measure [Product. Units] Cells

PART 2 — PROCESS CHARACTERISTICS

A-6 [Output. Rate] (Not Thruput) 200 Units (given on line A-5) Per Operating Minute

A-7 [Inprocess. Inventory. Time] 5m Calendar Minutes (Used only to compute in-process inventory)

A-8 [Duty. Cycle] .99 Operating Minutes Per Minute

A-8a [Number. Of. Shifts. Per. Day] Shifts

A-8b [Personnel. Integerization. Override. Switch] (Off or On)

PART 3 — EQUIPMENT COST FACTORS (Machine Description)

A-9 Component [Referent] Furnace

A-9a Component [Descriptive. Name]

A-10 Base Year For Equipment Prices [Price. Year] 1977

A-11 [Purchase. Cost. Vs. Quantity. Bought. Table] (Number Of and \$ Per Component) \$35K

A-12 Anticipated [Useful. Life] (Years) 7

A-13 [Salvage. Value] (\$ Per Component) \$3.5K

A-14 [Removal. And. Installation. Cost] (\$/Component) \$1k

Note: The SAMIS computer program also prompts for the [Payment. Float. Interval], the [Inflation. Rate. Table], the [Equipment. Tax. Depreciation. Method], and the [Equipment. Book. Depreciation. Method]. In the LSA SAMICS context, use 0.0, (1975 6.0 *), DDB, and SL. (The asterisk is a signal to the computer, not a reference to a footnote.)

A-15 Process Referent (From Front Side Line A-1) SINTERB

PART 4 - DIRECT REQUIREMENTS PER MACHINE (Facilities) OR PER MACHINE PER SHIFT (Personnel)

(Facility, Or, Personnel Requirement)

A-16 Catalog Number (Expense Item Referent)	A-18 Amount Required Per Machine (Per Shift) (Amount. Per. Machine)	A-19 Units	A-17 Requirement Description or Name
A2064D	132	Sq. Ft.	Mfg. Space (Type A)
B3672D	1	Person/Shift	Chemical Operator II 55885
B3688D	.05	Person/Shift	Electronics Maintenance

PART 5 – DIRECT REQUIREMENTS PER MACHINE PER MINUTE (SAMIS will ask first for Byproducts)

[Byproduct] and [Utility, Or, Commodity Requirement]

A-20 Catalog Number (Expense Item Referent)	A-22 Amount Required Per Machine Per Minute (Amount, Per, Cycle)	A-23 Units	A-21 Requirement Description or Name
EZ0102D	1.4124	Cu.Ft./Min	Nitrogen Gas
C1032B	.1258	KWh/Min.	Electricity
D1176D	-2	Cells/Min.	Rejected Cells

PART 6 - INTRA-INDUSTRY PRODUCT(S) REQUIRED

A-24 [Required Product] (Reference)	A-28 [Yield] (%)	A-26 [Ideal Ratio] Of Units Out/Units In	A-27 Units Of A-26***	A-25 Product Name
WAFERD	100	1.0	Cells/Wafers	Sintered Cells

PHILIP BLOOM

DAVID P. TANNER

TUDATE

9/16/80

*100% minus percentage of required product lost in this process.

**Assume 100% yield here.

**Examples: Modules/Cell or Cells/Wafer.

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D. COSTING

Using the IPEG costing method, the costs of the process were estimated. A one megawatt production level was chosen which uses 14% efficient solar cells. This would be 1,567,399 solar cell generating .638 watts per cell. The cost in 1980 dollars would be 7.93¢/cell or 12.4¢/watt. In 1975 dollars this translates to 5.87¢/cell or 8.19¢/watt. This cost does include the masking step as well as the plating cost. The masking step alone yields a cost of 2.3¢/watt in 1980 dollars or 1.7¢/watt in 1975 dollars.

E. CONCLUSIONS AND RECOMMENDATIONS

The 1980 cost of the masking steps (2.3¢/watt) comes from high equipment cost and high material cost of running the screen printing equipment. Notice, these costs come from a relatively low throughput and the high operational cost of the screen printer and not from the high cost of the plating mask resist. The resist only accounted for 20% of these costs (.5¢/watt). It is very probable that further work with a screen printer equipment vendor could result in a much lower cost for our operation. The other major cost in the process is the copper electrolytic plating due to the low throughput assumed. (High labor costs.) This cost also could be reduced with working with a plating equipment vendor.

The most desirable method of reducing the cost would be the elimination of the palladium bath step. If an adherent nickel bath could be found, the palladium step and one sintering step could be removed. Assuming the new nickel bath would cost approximately the same as the existing nickel bath, the cost of the process would be lowered by 2.3¢/watt in 1980 dollars. With lowering the cost of the masking steps by 50% and lowering the copper plating cost by 30% this should yield a final cost of 7.83¢/watt in 1980 dollars.

APPENDIX

COST CALCULATIONS

PROCESS: Pdplate

Each hood has 6 tanks requiring 2.106 gallons of solution to fill. Each process step utilizes 2 tanks in a particular hood. The 6% HF solution used is assumed to be replaced once every shift. The palladium solution is replaced as a whole once per shift, but the PdCL is replenished as needed. Rinse water requirements is 3 gal./min. for each hood. The 2% NaOH solution is replaced every hour and the IPA bath is replaced every 4 hours.

A) HF Usage:

$$4.212 \text{ gal/shift} \times .06 (\% \text{HF}) = .2527 \text{ gal/shift}$$

$$.2527 \text{ gal/shift} \times 9.75 \frac{\text{lb}}{\text{gal}} (\text{HF}) \times \text{shift/480 min.} = 00513 \frac{\text{lb.}}{\text{min.}}$$

DI H_2O usage for this step = .0011 cuft/min.

B) Pd Bath:

Assuming 110% contact coverage 50A thick yields:

$$1.1 \times \frac{(7.6)^2}{4} \frac{\text{cm}^2}{\text{cm}^2} \times \frac{6.08 \times 10^{-6} \text{g}}{\text{cm}^2} \times \frac{172.3 \text{g PdCl}_3}{106.4 \text{gm Pd}} = .0051 \text{ gm/wafer}$$

with 400 wafer/12m yields .0168 $\frac{\text{gm}}{\text{min.}}$

The 2.106 gal solution is replaced as a whole every shift (8 hrs.) so HCL used is 50 ml, NH_4F used is 994 ml, and DI H_2O used is 1.49 liters.

$$HCL = .1042 \text{ ml/min} \times 1.0045 \text{ gms/ml.} \times 2.205 \times 10^{-3} \text{ lb/gm} = .00023 \text{ lb/min.}$$

$$NH_4F = 2.071 \text{ ml/m} \times 1.009 \text{ gm/ml} \times 2.205 \times 10^{-3} \text{ lb/gm} = .004601 \text{ lg/min.}$$

$$H_2O = .00011 \text{ cuft/min.}$$

c) NaOH Bath (2% Solution)

This bath is replaced once every hour:

$$4.212 \text{ gal/hr.} \times .0702 \text{ gal/min.} \times 3.785 = .2657 \text{ liter/min} \times 2\% = .005314 \text{ liter/min.}$$

$$\approx .00514 \text{ gm/min} \times 2.205 \times 10^{-3} \text{ lb/gm}$$

$$\approx .000012 \text{ lbs/min}$$

DI H Usage .00919 cuft/min.

D) IPA Baths

These baths are assumed to be replaced every 4 hours:

$$4.212 \text{ gal/4hrs.} \approx .0176 \text{ gal/min.}$$

E) Hood With Replenish System Electrical Assumed Usage is:

1.6 KW and 500 cfm air use of only 50% panel value

$$\left[.5 (1.1) + 450 \text{ CFM} \frac{.46 \text{ kw}}{1000 \text{ cfm}} \right] \times \frac{8766 \text{ hr.}}{\text{Year}} \div \frac{245 \text{ Day}}{\text{Year}} \div \frac{24 \text{ hr.}}{\text{Day}} \div \frac{60 \text{ min.}}{\text{Hr.}} \\ = .01881 \text{ KWH/MIN.}$$

$$\left[.5 (1.6) + 500 \frac{46}{1000} \right] \times \frac{8766 \text{ hr.}}{\text{Year}} / 245 \times 24 \times 60 = .02559 \text{ KWH/MIN.}$$

$$\text{TOTAL: } .01881 \text{ KWH/MIN} + .02559 \text{ KWH/MIN} = .0444 \frac{\text{KWH}}{\text{MIN}}$$

TOTAL DI H₂O - .00919 cuft/min.

.00110 "

.00110 "

.01139 cuft/min.

Each hood used 3 gal/min. rinse water

$$2 \text{ hoods} \approx 6 \text{ gal/m} \times 1.337 \times 10^{-1} \text{ cuft/gal} = .802 \text{ cuft/min.}$$

$$\text{TOTAL: } .81339 \text{ Cuft/min.}$$

APPENDIX L

DEVELOPMENT OF LOW COST CONTACTS TO SILICON SOLAR CELLS

"ANALYSIS OF COPPER DIFFUSION
THROUGH DIFFERENT METALLIC BARRIERS"

JPL CONTRACT NO. 955244

29 OCTOBER 1979

BY DAVID TANNER

OPTICAL COATING LABORATORY, INC.
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15251 EAST DON JULIAN ROAD
CITY OF INDUSTRY, CA 91746

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INTRODUCTION

This contract involves the evaluation of the technical feasibility and effective cost of a copper plating system for the manufacture of solar cells for high volume production of low cost solar array (LSA) modules.

The first phase of the contract (October 1978 - May 1979) a procedure was developed to plate copper onto solar cells for use as a low cost electrical contact. The contact system first used an electroless palladium bath (50 \AA), next an electroless chromium bath (~2000 \AA), an electroless copper bath (500 \AA), and then an electrolytic copper bath (4-5 microns). This contact system has produced cells with good I-V characteristics as well as good contact adhesion [1]. However, it was found if the cells were heated to 400°C for 5 minutes they would severely degrade. The problem was speculated to be copper migration into the cell [2].

The second phase of the contract (July 1979 - January 1980) has sought means to stop the copper migration. This paper is a literature study of copper diffusion rates through different metallic barriers. Though only metals that can be plated are of interest with our process, other metals will be discussed for completeness. Finally given is a test matrix of metals to be used in the next task of the contract, an evaporated contact heat treat study.

DISCUSSION

A literature search has been conducted in order to locate papers dealing with copper diffusion and/or interactions with different metallic barriers. It was preferred that the search be restricted to papers dealing strictly with diffusion studies using thin films. But during the search it became obvious that only a limited amount of data on thin films is available. Most sources use bulk samples in polycrystalline or crystalline form. The papers used a variety of techniques of measuring copper diffusion ranging from radioactive tracer experiments to use of an electron microprobe. Each diffusion measurement technique will be identified in the text, but will be ignored in the final data assembly due to the limited data base of this study.

Data have been found on these different metal systems: Cu \rightarrow Ag, Cu \rightarrow Au, Cu \rightarrow Be, Cu \rightarrow Cr, Cr \rightarrow Cu, Cu \rightarrow Fe, Cu \rightarrow Li, Cu \rightarrow Ni, Cu \rightarrow Pd, Pd \rightarrow Cu, Cu \rightarrow Pt, Cu \rightarrow Sb, Cu \rightarrow Ti, Cu \rightarrow U and Cu \rightarrow Zr. Also two papers were found on the Cr-Cu contact system, mainly dealing with contact stability.

As stated in the introduction, an evaporated contact study will be conducted to test the conclusions from the paper study. It is realized that plated metal layers are usually less dense than evaporated layers and the results from the evaporation study may not apply to the plated layers. Hopefully the tests can guide future research of plating metals.

RESULTS

Copper Diffusion Into Metals

A summary of the diffusion data is given in Figure 1. The dotted lines are extensions of the actual data (solid lines) from the different publications. The particulars of each diffusion system and the publication details are given next.

(i) Cu-Ag

The work was done by Sawatzby and Jaunot [3] in 1957. Single crystals of silver were diffused with the radioisotope ^{64}Cu over a temperature range of 700-900°C. The samples were sectioned and the radioactive counts taken.

(ii) Cu-Au

This data was generated by Vignes and Haeussler [4] in 1966. Bulk polycrystalline gold sample were used with a 2μ layer (evaporated) of pure copper on the surface. The copper was diffused over a temperature range of 700-900°C and analyzed by a electron microprobe.

(iii) Cu-Be

The copper diffusion into beryllium was taken from work done by Dupouy, Mathle, and Adda in 1965 [5]. Radioactive ^{64}Cu was diffused into single crystal beryllium over a temperature range of 700-1050°C.

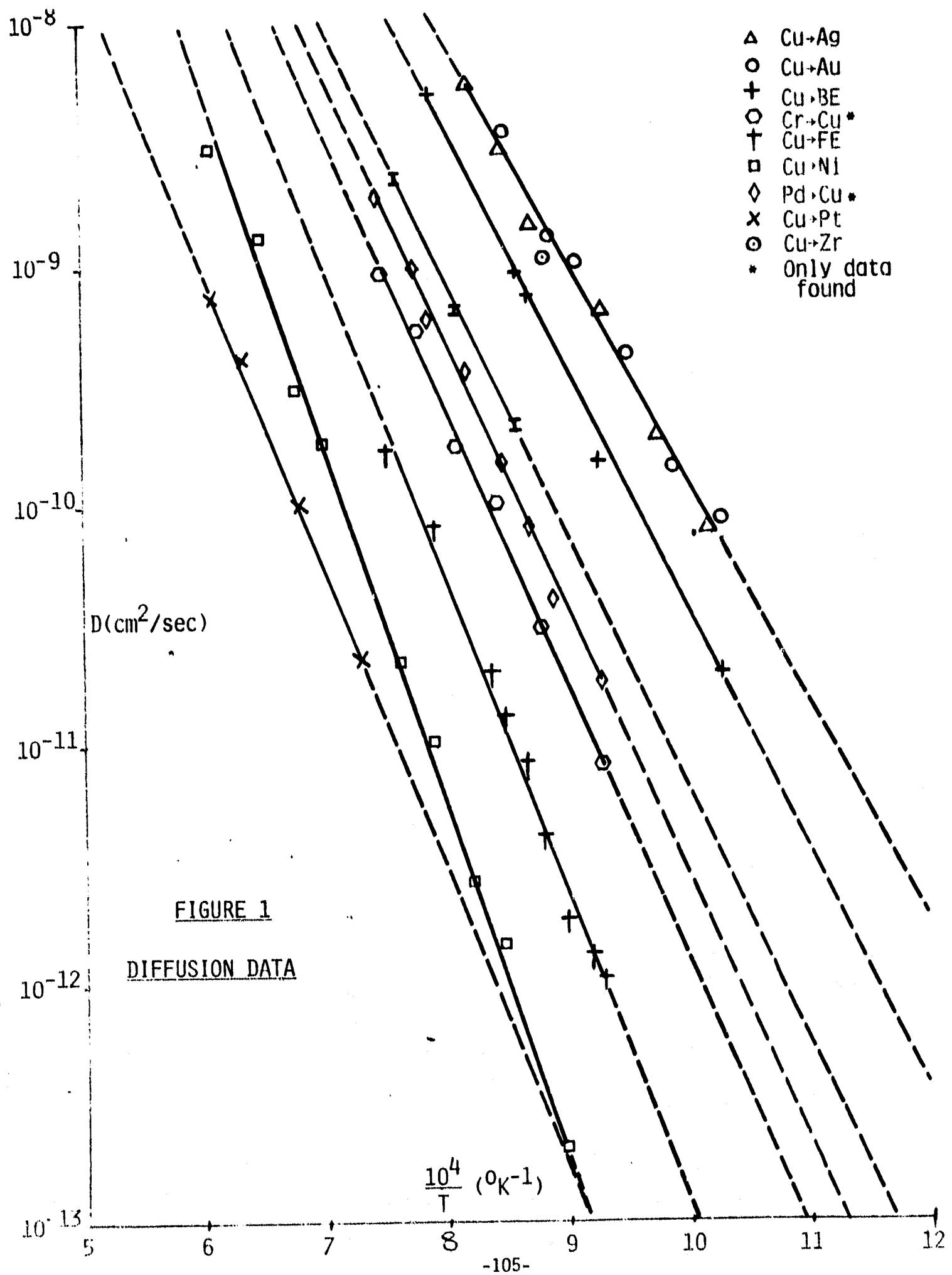


FIGURE 1

DIFFUSION DATA

(iv) Cu-Cr and Cr-Cu

Only qualitative estimates were found on the measurement of Cu-Cr. Some papers were found on the thin film interdiffusion of this system [6] as well as papers dealing with silicon device performance of the Cr-Cu system [7], [8]. The interdiffusion study showed there was little interaction of the metals over the temperature range of 550-750°C. The device data also indicated the diffusion rate was relatively slow. However, a paper was found on the diffusion of Cr-Cu using ^{51}Cr with a sample of pure polycrystalline copper. This work was taken from Seitz [9] (1963), Tomizuke [10] (1971), Barreau [11] (1971), and Sexena [12] (1971). Since this measurement is not the same as Cu-Cr, an asterisk is added on Figure 1.

(v) Cu-Fe

This data came from a paper by Anand [13] published in 1966. Again the radioisotope ^{64}Cu was diffused into a sample of pure polycrystalline iron and the diffusion coefficients measured (temperature range was 750-1050°C).

(vi) Cu-Li

This paper stated the results of the diffusion of ^{64}Cu into a pure sample of polycrystalline lithium by Ott [14], [15] in 1969. The heat treatments were only over a range of 50-120°C since the diffusion rate was so high. The diffusion rate

was much faster than for the other samples, so the data will not be plotted on Figure 1. The diffusion coefficient $D^*(\text{cm}^2/\text{sec.})$ ranged from 3×10^{-7} at 120°C to 2.7×10^{-8} at 50°C .

(vii) Cu-Ni

This uses the results of Monma [16] (1964) and Helfmeier [17] (1970) using the ^{64}Cu technique and thin film microprobe technique respectively. In both cases polycrystalline nickel was used. The diffusions were done over a temperature range of 700 - 1400°C . The data of both sources were combined for the Figure 1 plot.

(viii) Cu-Pd and Pd-Cu

It was difficult to find details of Cu diffusion into palladium. Westinghouse [18], made a number of solar cells using Pd-Cu contacts. Using only mild heat treatments ($\sim 300^\circ\text{C}$ for 15 minutes), all test cells degraded severely. This would indicate the diffusion rate of copper through evaporated palladium is quite fast. There were other data showing the diffusion of palladium through crystalline copper is very fast [19]. This was taken from Peterson's paper published in 1963. For qualitative comparison, these results are included in Figure 1, for the same reason as including the Cr-data.

(ix) Cu-Pt

In this paper by Johnson [20] in 1963 tracer diffusion of ^{64}Cu was made into a sample of polycrystalline platinum over a

temperature range of 1000-1500°C. From the data plotted in Figure 1, this appears to be one of the best barriers to the copper diffusion.

(x) Cu→Sb

This study of the tracer diffusion of ^{64}Cu into pure antimony was made by Heumann [21] in 1956. The results at 390°C yielded a diffusion coefficient of $\sim 10^{-4} \text{ cm}^2/\text{sec}$. which off the scale used for Figure 1.

(xi) Cu→Ti

The diffusion of Cu into β -Ti was made by Caloni in 1969 [22]. Over a temperature range of 960-1460°C an evaporative film of copper was diffused into polycrystalline samples of titanium. An electron microprobe was used for the analysis. These data were also off the scale of Figure 1 because the copper diffused very quickly in β -titanium. At 960°C (which is about 8 on the $10^4/\text{T}^\circ\text{K}$ scale) the diffusion coefficient was $10^{-8} \text{ cm}^2/\text{sec}$.

(xii) Cu→U

The diffusion of copper into α (b.c.c.) uranium has been measured from 780-1080°C by Peterson [23], [24] in 1964. ^{64}Cu was diffused and the radioactive tracer diffusion coefficients measured.

These data also were not plotted on Figure 1 because the diffusion rates were too high. At 780°C ($10^4/\text{T}^\circ\text{K}$ reading of 9.5) the diffusion coefficient was $2 \times 10^{-8} \text{ cm}^2/\text{sec}$.

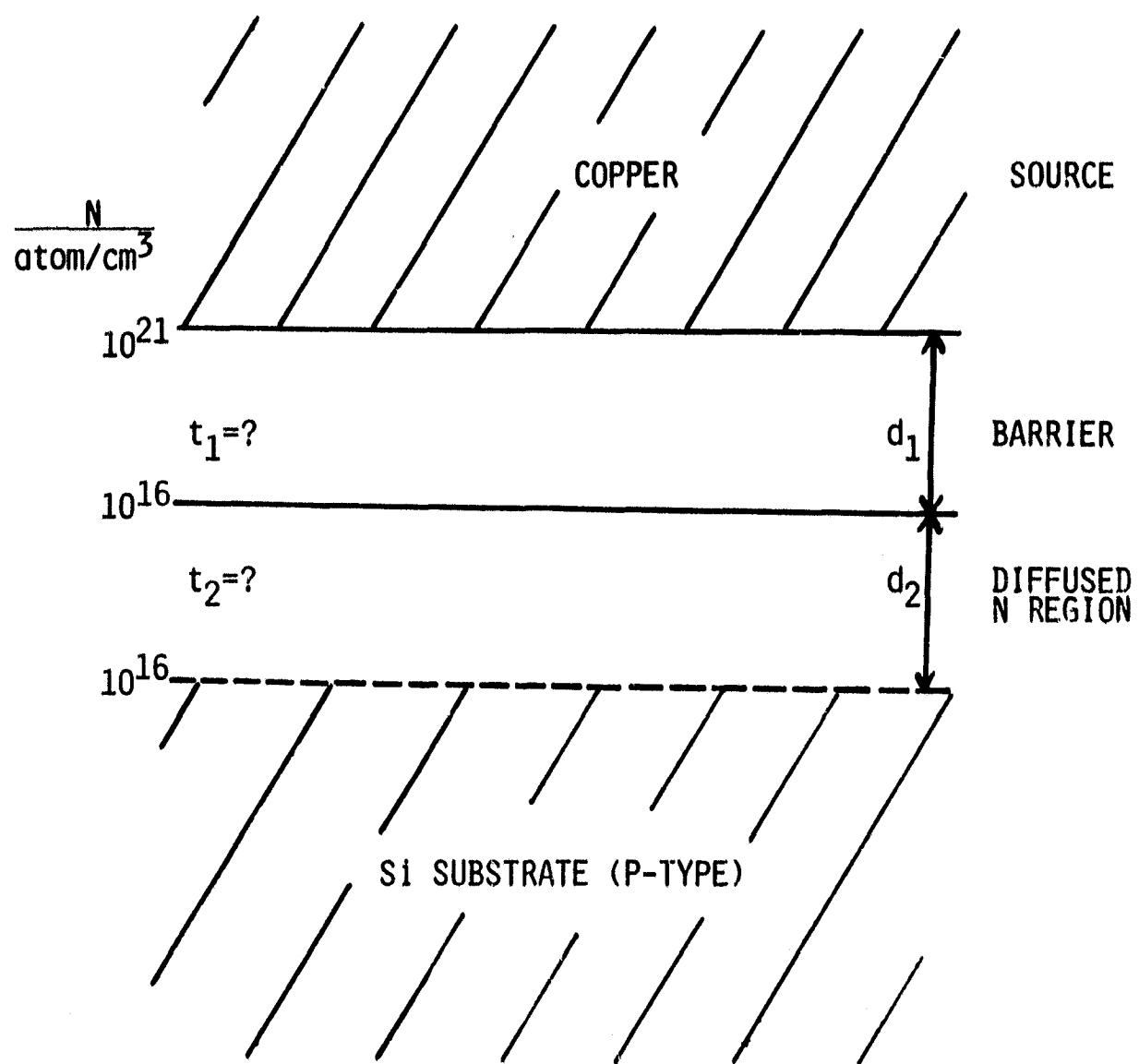
(xiii) Cu \rightarrow Zr

The tracer diffusion of ^{64}Cu was made into single crystal of α -zirconium by Hood in 1971 [25]. The measurements were only made at 865°C, yielding a diffusion coefficient $\sim 10^{-8} \text{ cm}^2/\text{sec.}$

ANALYSIS

Using the data found in the literature study, diffusion rate calculations, using a single mode system were made. The major part of the proposed evaporated contact heat treat study was to observe solar cell degradation. It has been previously shown that the diffusion of copper causes shunting problems with silicon solar cells (lowering of V_{OC}) [2]. At the 13th JPL Project Integration Meeting, Westinghouse [26] showed that copper at reasonably high levels (10^{16} - 10^{17} atom/cm³ in P-type silicon) was needed before any degradation would be seen. Therefore it was assumed that when the cell degraded, the copper would have reached a concentration of 10^{16} atom/cm³ at the junction (N/P interface). Figure 2 shows the diffusion model used in this analysis. The source in the model was the copper layer (typically 4-6 microns thick). The barrier was any metal which would provide a good barrier to the copper and a good electrical contact to the silicon. The barrier thickness was demoted as d_1 . The diffused n region was the thickness d_2 of the silicon cell (the junction depth). The qualities we were interested in calculating were t_1 the diffusion time through the barrier and t_2 the diffusion time to the junction. The total diffusion time $t_{TOTAL} = t_1 + t_2$ was set up as the time it takes for the junction interface (N/P interface) to reach a copper concentration of 10^{16} atom/cm³. Using the standard single mode diffusion analysis; (Fick's laws of diffusion [27])

$$\text{Equation 1: } N(x,t) = N_{cu} \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right)$$



DIFFUSION MODEL

FIGURE 2

where x = thickness
 D = diffusion coefficient
 t = diffusion time
 N_{Cu} = concentration of copper atoms
 $N(x,t)$ = the resultant copper diffusion concentration at x after time t

The values of N_{Cu} at the barrier surface was assumed to be 10^{21} atom/cm³.

The value of $N(x,t)$ was also assumed leaving the diffusion time as the only variable. By setting a $N(d_1, t_1)$ to be 10^{16} atom/cm³, the diffusion time for nickel barrier using the data from Figure 1 was solved.

The diffusion coefficient for nickel at 560°C was extrapolated to be 1.4×10^{-17} cm²/sec. Using a nickel thickness of 1000 \AA , the resultant diffusion time t_1 was 1.83×10^5 sec or 127 days. So it would take more than four (4) months for the copper to get through the nickel barrier.

Certainly this was an experimentally acceptable length of time and suggests that at normal operating temperatures, the cell lifetime would be good.

To calculate the diffusion time t_2 a simular calculation was done using the 10^{16} atom/cm³ number as N_{Cu} . As stated before the shunting copper level was 10^{16} atom/cm³ which becomes $N(d_2, t_2)$ in this case. From Runyan's book [27] at 560°C the diffusion coefficient of copper in silicon was 2×10^{-5} cm²/sec. Using a junction thickness of 3000 \AA (d_2) the diffusion time t_2 was calculated to be 40 ms. Since $t_1 \gg t_2$, the total diffusion time ($t_T = t_1 + t_2$) becomes $t_T = t_1$. This shows that barrier must do all the work in stopping the copper diffusion.

Assuming that extrapolation of the diffusion rate can be carried to lower temperatures, estimates show that at 60°C the diffusion of copper through the same nickel barrier would take $\sim 10^{18}$ years. However, the analysis used was very restricted and does not include,

- (a) Possibility of variable barrier thicknesses, pinholes, or severe structural defects in the layer.
- (b) Chance of alternate penetration modes (around edges of the plated or evaporated layers).
- (c) Possibility of degradation from impurities other than copper.

A similar diffusion analysis for silver (the worst barrier) yields a diffusion time at 560°C of .3 seconds. Certainly the diffusion data does realistically indicate that nickel is a promising platable diffusion barrier to copper and should be investigated further.

CONCLUSION

From the literature study, nickel appears to be the best platable candidate for a metallic barrier to the copper migration. Since nickel is relatively cheap and a number of commercially obtainable electroless baths already exist, it can be readily incorporated into the present plating process. The next step is to see if nickel has good barrier properties experimentally. This will be done by an evaporated contact study using active solar cells. The barrier metal experiment will use the metals in different thicknesses over a range of heat treatments. The degradation of the cells voltage and current will be evaluated. The test matrix is given below, and will be used for the following condition.

- (i) All heat treatments will be made in nitrogen only.
- (ii) Properties of the solar cells will be evaluated before and after the heat treatments.
- (iii) Heat Treatments

<u>TIME</u> (Minutes)	<u>TEMPERATURE</u> (°C)				
5	400	450	500	550	600
15	400	450	500	550	600

- (iv) All tests will be run with two control cells with Ti-Pd-Ag contacts.
- (v) The following metallization systems will be investigated.

- (A) Pd-Ag (2000 \AA Pd): To study effects of palladium only.
- (B) Cr-Ag (2000 \AA Cr): To study effects of chromium only.
- (C) Pd-Cu: Three different experiments using 1000-2000-3000 \AA of Pd.
- (D) Cr-Cu: Three different experiments using 1000-2000-3000 \AA of Cr.
- (E) Pd-Ni-Cu (1000 \AA Pd): Two experiments with the nickel at 1000 and 2000 \AA thick.
- (F) Cr-Ni-Cu: The same as (E) but using 1000 \AA chromium.

Hopefully these evaporated metal heat studies will give us some insight experimentally on the quality of the nickel barrier. Of course with a plated nickel barrier, the results may not be as good (plated metals are less dense). But hopefully the barrier thickness can be adjusted to give the desired result, of a reliable copper based solar cell contact.

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NOTE: Many of the references were taken from J. Phys. Chem. Ref. Data, ("Diffusion of Copper and Copper Alloys") 3, 4, 5, 6, (1974), (1975), (1976) and (1977).